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1989

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CATALOGING PREP

DYEING AND FINISHING TASK FORCE

TEXTILE FINISHING CHEMISTRY RESEARCH UNIT

SOUTHERN REGIONAL RESEARCH CENTER

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JUNE 29-30, 1989

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AGENDA

1989 DYEING AND FINISHING TASK FORCE

TEXTILE FINISHING CHEMISTRY RESEARCH UNIT SOUTHERN REGIONAL RESEARCH CENTER

P. O. Box 19687
New Orleans, Louisiana 70179

THURSDAY, JUNE 29, 1989

9:00 AM	Welcome to SRRC	Noelie R. Bertoniere Research Leader
9:05	Overview of Cotton Research in ARS	F. X. Werber National Program Leader, Fibers
9:15	Overview of Textile Finishing Chemistry Research Unit	N. R. Bertoniere Research Leader

CELLULOSE STRUCTURE

9:20	Pore Structure of Fabrics Crosslinked with Formaldehyde-Free Esters	N. R. Bertoniere
10:00	Coffee	

LOW/NO FORMALDEHYDE DURABLE PRESS

10:20	Post Dyeing of Formaldehyde-Free Ester Crosslinked Cotton Fabrics	B. K. Andrews
11:00	Thermal Decomposition of Polycarboxylic Acids	B. J. Morrell
11:40	Catalysts for High-Speed Esterification of Cellulose	C. M. Welch
12:20 PM	Lunch	

TEMPERATURE ADAPTABLE FABRICS

1:00 PM	Fixation of Polyethylene Glycol via a Low Temperature Cure	T. L. Vigo
1:40	FTIR Characterization of Fabrics Containing Crosslinked Polyethylene Glycols	N. M. Morris
2:20	Improved Process for Treating Cotton Fabrics with Crosslinked Polyols	J. S. Bruno
3:00	Coffee	

IMPROVED DURABLE PRESS

3:20	Cationic Finishes for Garment Dyeing	R. J. Harper, Jr.
4:00	Single Sided Treatments via Foam Finishing	A. H. Lambert
4:40	Low Wet Add-on Finishing with BTCA	C. E. Morris
7:00	Banquet, Upperline Restaurant, 1413 Upperline (just off St. Charles on the river side)	

FRIDAY, JUNE 30, 1989

GARMENT DYEING

9:00 AM	Dyeability of Cotton Fabric Treated with Carbamoylethylamine Adducts	R. M. Reinhardt
9:40	Recent Advances in the Use of Amine Additives to Improve Dyeability of Crosslinked Cotton	E. J. Blanchard
10:20	Coffee	

COTTON NONWOVENS

10:40	Current Status of Research on Cotton Nonwovens	J. P. Moreau
11:20	GENERAL DISCUSSION	
12:00	ADJOURN	

TEXTILE FINISHING CHEMISTRY RESEARCH UNIT

IMPROVED DURABLE PRESS FABRICS

Robert J. Harper, Jr.

Allan H. Lambert

Cletus Morris

CELLULOSE STRUCTURE/STRENGTH RETENTION

Noelie R. Bertoniere

DYEABLE DURABLE PRESS FABRICS

Robert M. Reinhardt

Eugene J. Blanchard

TEMPERATURE ADAPTABLE FABRICS

Tyrone L. Vigo

Nancy Morris

Joseph S. Bruno

LOW/NO FORMALDEHYDE

Bethlehem K. Andrews

Clark M. Welch

Brenda J. Morrell

COTTON-CONTAINING NONWOVENS

Jerry P. Moreau

Research Associate

Pore Structure of Fabrics Crosslinked with Formaldehyde-Free Reagents

Noelie R. Bertoniere and Walter D. King

The pore structures of cotton fabric crosslinked with several formaldehyde-free durable press reagents were elucidated. Results were compared with those for the industry standard, DMDHEU. The structure and application conditions for DMDHEU are given in slides 1 and 2. The formaldehyde-free reagents were BTCA (butanetetracarboxylic acid), DHDMI (dihydroxydimethylimidazolidinone), and the glyoxal/glycol system. Their structures and application conditions are given in slides 3-9. The fabric was an 80 x 80 cotton printcloth. Treatments were designed to impart the same degree of conditioned wrinkle recovery (WRA) to the fabric. The degree to which we were successful is given in slide 10 which also includes the wet wrinkle recovery angles. Comparable levels of conditioned WRA were realized for all but the DHDMI sample. Several attempts were made to raise the value to the 253-265°(W+F) range but were unsuccessful. It had been demonstrated earlier by J. G. Frick that this reagent imparts intralamellar, but not interlamellar, crosslinking in the crystalline cotton fiber. The technique he employed was that of methacrylate expansion; the DHDMI treated sample expanded in a manner similar to unmodified cotton whereas DMDHEU treated samples were inert. DMDHEU gives in both interlamellar and intralamellar crosslinks. Also notable in slide 10 is the high wet wrinkle recovery angle realized with DMDHEU. The accompanying strength properties are given in slide 11. The highest levels of retained breaking strength were found in the BTCA and DHDMI samples; it must be noted that the latter had a lower degree of resilience as measured by conditioned WRA. The glyoxal/glycol treated sample retained a lower level of breaking strength. Retentions of elongation-at-break were comparable. Tearing strength retention followed the same pattern as breaking strength retention. The abrasion resistance properties are summarized in slide 12. Retention of Stoll flex abrasion resistance was greater in the BTCA and DHDMI treated fabrics; again it must be remembered that DHDMI imparted a lower level of resilience. Accelerator abrasion weight loss was over 10% for both glyoxal/glycol and BTCA but only 8.3% for the DMDHEU treated fabric. This is the one instance where BTCA did not outperform DMDHEU when the reagents were applied to give the same conditioned WRA.

The general principles of gel permeation chromatograph are illustrated in slide 13. Case A depicts the case of very small molecules that can penetrate pores of all sizes. Case B depicts intermediate size molecules that enter some, but not all, of the

pores. Case C depicts a very large molecule that is excluded from all internal pores. Examples of these three circumstances are water (Case A), most finishing agents and the probes used in this study (Case B), and high molecular weight polymers such as Dextran T-40 used to determine the void volume of the column (Case C). The pore size distributions of the cottons were assessed via the reverse gel permeation chromatography technique.

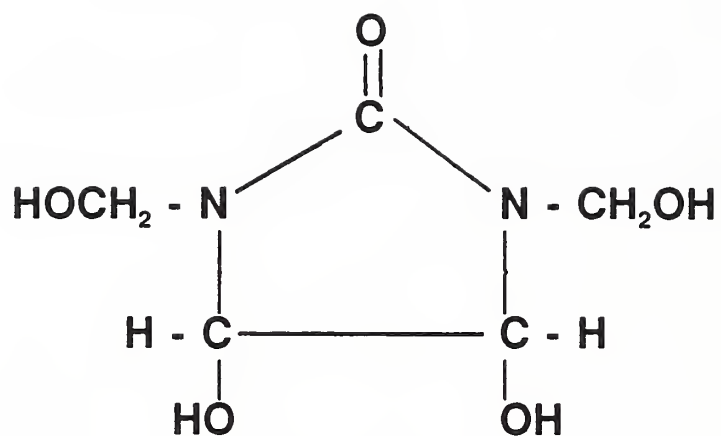
The columns were precision bore (2.54 cm x 45-50 cm between top and bottom bed supports). The cotton fabrics were successively passed through 20, 40, 60 and 80 mesh screens in a Wiley mill. The ground fabric was placed in water and the slurry degassed. The columns were prepared by settling the cotton slurries through an extension tube in the conventional manner. The solutes, which are shown in slides 14-16, used as molecular probes were applied individually as 2% solutions through a 0.5 ml sample loop. The flow rate was 26 ml/cm²/h. The eluate was monitored continuously with a differential refractometer. Elution volumes were determined gravimetrically by collecting the eluate in tared test tubes and summing the weights of fractions and proportional parts of fractions between the injection and the peak of the recorded elution curve for each solute. Gel permeation chromatographic results were obtained in terms of the parameters defined in slides 17 and 18. V_i 's, the averages of six replicates having standard deviations from 0.001 to 0.012, were fit to straight lines via the methods of linear least squares. Plots were prepared of V_i , the accessible internal water, versus the molecular diameters of the probes. These are shown in slides 19, 20 and 21 for the sugars, ethylene glycols and glymes, respectively. Crosslinking effected a decreased in accessible internal volume across all pore volumes with all four reagents. The greatest decrease was effected by DMDHEU. Treatment with BTCA to the same level of crease recovery effected a notable lower loss of internal volume. Crosslinking with DHDMI caused the least amount of internal structure collapse but again it must be pointed out that this sample had a lower degree of resilience.

Moisture regain, considered to be a measure of the internal surface of the cotton fiber in the conditioned state, was determined on the five samples. The results are assembled in slide 22. Crosslinking with DMDHEU, BTCA and glyoxal/glycol decreased moisture regain. The greatest decrease occurred with DMDHEU. Water of imbibition was also determined. This is a measure in the internal fiber volume in the water swollen state. These results are assembled in slide 23. Crosslinking with all of the reagents reduced this property. The greatest reduction was with DMDHEU.

A property similar, but not identical, to water of imbibition is V_2 , which is taken from the curve in slide 19 and defined in slide 18. It is the internal water available as

solvent for a very small molecule, i.e., water. The value 2 for the molecular diameter of water was taken from Drieding models. Changes in V_2 are indicative of changes in very small pores. These results are given in slide 24. Differences among the samples are greater than for water of imbibition. The lowest value was observed with the DMDHEU sample, generally comparable values were realized for BTCA and glyoxal/glycol samples. The highest value was for DHDMI treated fabric but this sample had a lower level of resilience. Another parameter derived from the plots in slide 19, also defined in slide 18, is the permeability limit, M_l which is size of the smallest molecule that is totally excluded from the interior of the cotton fiber. It is the intercept on the X-axis where $Y = 0$. These data, a measure of the changes that have taken place in large pores, are assembled in slide 25. Again the largest decreased was effected by crosslinking with DMDHEU, BTCA and glyoxal/glycol were comparable, and the lowest decreased was with DHDMI.

Observations made in this study are summarized in slides 26-29. It was concluded (slide 30) that formaldehyde-free crosslinking reagents effect a lower level of collapse of the internal pore structure of the cotton fiber than does DMDHEU at generally comparable levels of resilience.



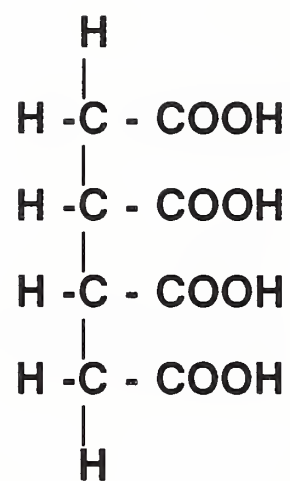
DMDHEU
(DIMETHYLOLDIHYDROXYETHYLENEUREA)

DMDHEU

FABRIC	COTTON PRINTCLOTH, 80x80
SOLUTION	6% DMDHEU 2.1% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

PROCESSING CONDITIONS

PAD	2 DIPS, 2 NIPS
DRY	10 MINUTES AT 70° C
CURE	3 MINUTES AT 160° C
MACHINE WASH	
TUMBLE DRY	



BTCA

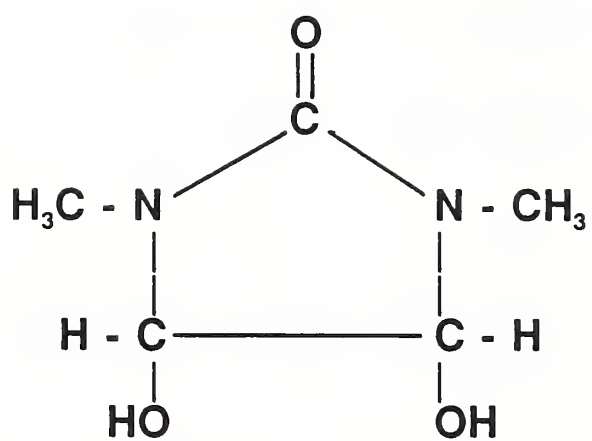
(BUTANETETRACARBOXYLIC ACID)

BTCA

FABRIC	COTTON PRINTCLOTH, 80x80
SOLUTION	9.5% BTCA 6.6% Na ₂ HPO ₄ (anhy)

PROCESSING CONDITIONS

PAD	2 DIPS, 2 NIPS
DRY	5 MINUTES AT 85° C
CURE	90 SECONDS AT 180° C
MACHINE WASH	
TUMBLE DRY	



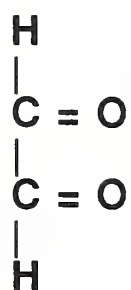
DHDMI
(DIHYDROXYDIMETHYLIMIDAZOLIDINONE)

DHDMI

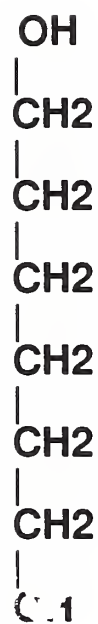
FABRIC	COTTON PRINTCLOTH, 80x80
SOLUTION	12% DHDMI 1.5% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid (20/1)

PROCESSING CONDITIONS

PAD	2 DIPS, 2 NIPS
DRY	7 MINUTES AT 70° C
CURE	3 MINUTES AT 160° C
MACHINE WASH	
TUMBLE DRY	



GLYOXAL



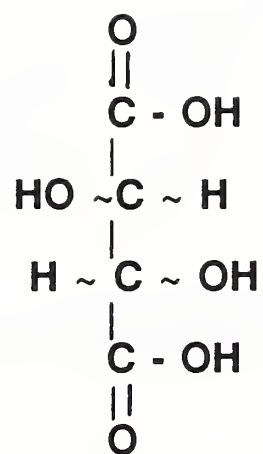
1, 6-HEXANEDIOL

GLYOXAL/GLYCOL

FABRIC	COTTON PRINTCLOTH, 80x80
SOLUTION	3.2% GLYOXAL 6.53% HEXANEDIOL 0.8% $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ 0.35% TARTARIC ACID 0.185% $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$

PROCESSING CONDITIONS

PAD	2 DIPS, 2 NIPS
DRY	5 MINUTES AT 85° C
CURE	3 MINUTES AT 120° C
MACHINE WASH	
TUMBLE DRY	



TARTARIC ACID

RESILIENCE

WRINKLE RECOVERY ANGLES °(W+F)

	CONDITIONED	WET
CONTROL	157	143
DMDHEU, 5%	265	244
BTCA	264	213
DHDMI	235	214
GLYOXAL/GLYCOL	253	214

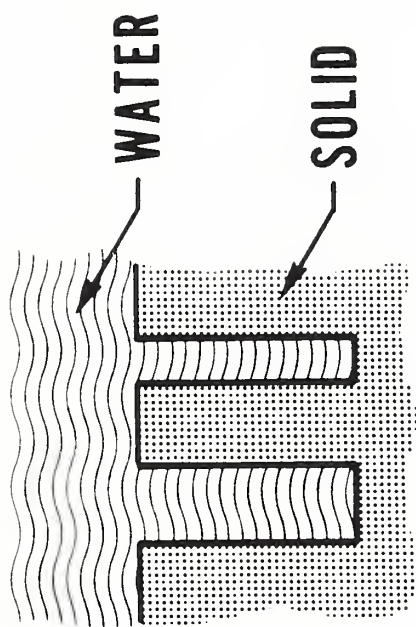
STRENGTH

	BREAK	ELONG.	TEAR
	% RETAINED		

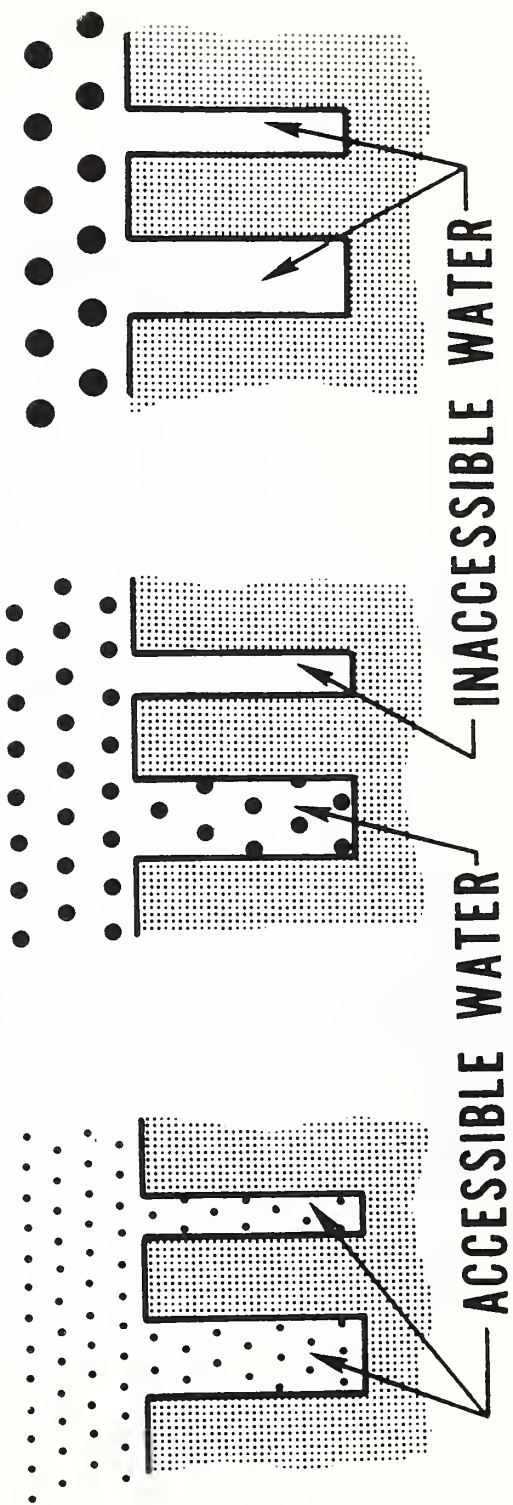
CONTROL	100	100	100
DMDHEU, 6%	55	44	52
BTCA	65	43	64
DHDMI	66	47	59
GLYOXAL/GLYCOL	43	42	38

ABRASION RESISTANCE

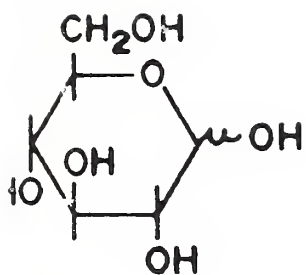
	STOLL FLEX	ACCELEROTOR
	% RETAINED	% WT. LOST
CONTROL	100	1.3
DMDHEU, 6%	25	8.3
BTCA	40	11.1
DHDMI	44	2.2
GLYOXAL/GLYCOL	27	12.4



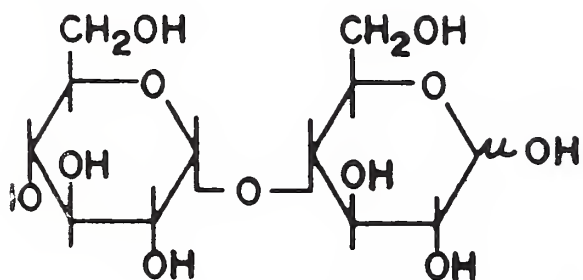
ADDITION OF
SOLUTION →



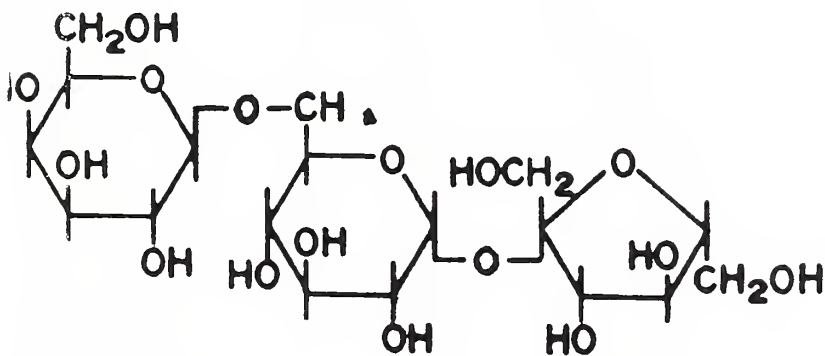
CASE A CASE B CASE C



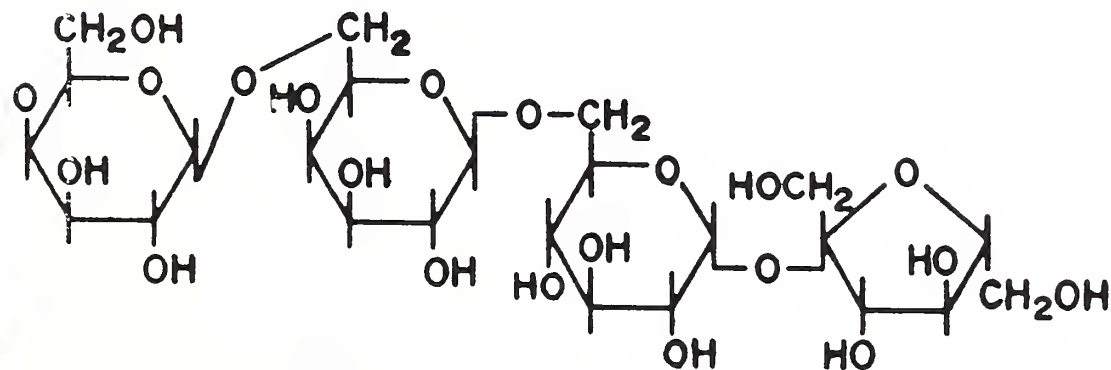
GLUCOSE
180



MALTOSE
342



RAFFINOSE
504



STACHYOSE
666

ETHYLENE GLYCOLS



GLYMES



$$V_i = (V_e - V_o)/W$$

$$V_g = (V_t - V_o)/W$$

$$V_w = V_g - 0.629$$

V_e	elution volume (ml)
V_o	void volume (ml) from Dextran T-40
W	weight of dry cellulose (g)
V_t	total column volume (ml)
V_i	accessible internal volume (ml/g)
V_g	specific gel volume (ml/g)
V_w	total internal water (ml/g)
0.629	specific volume of cellulose (ml/g)

CALCULATED VALUES

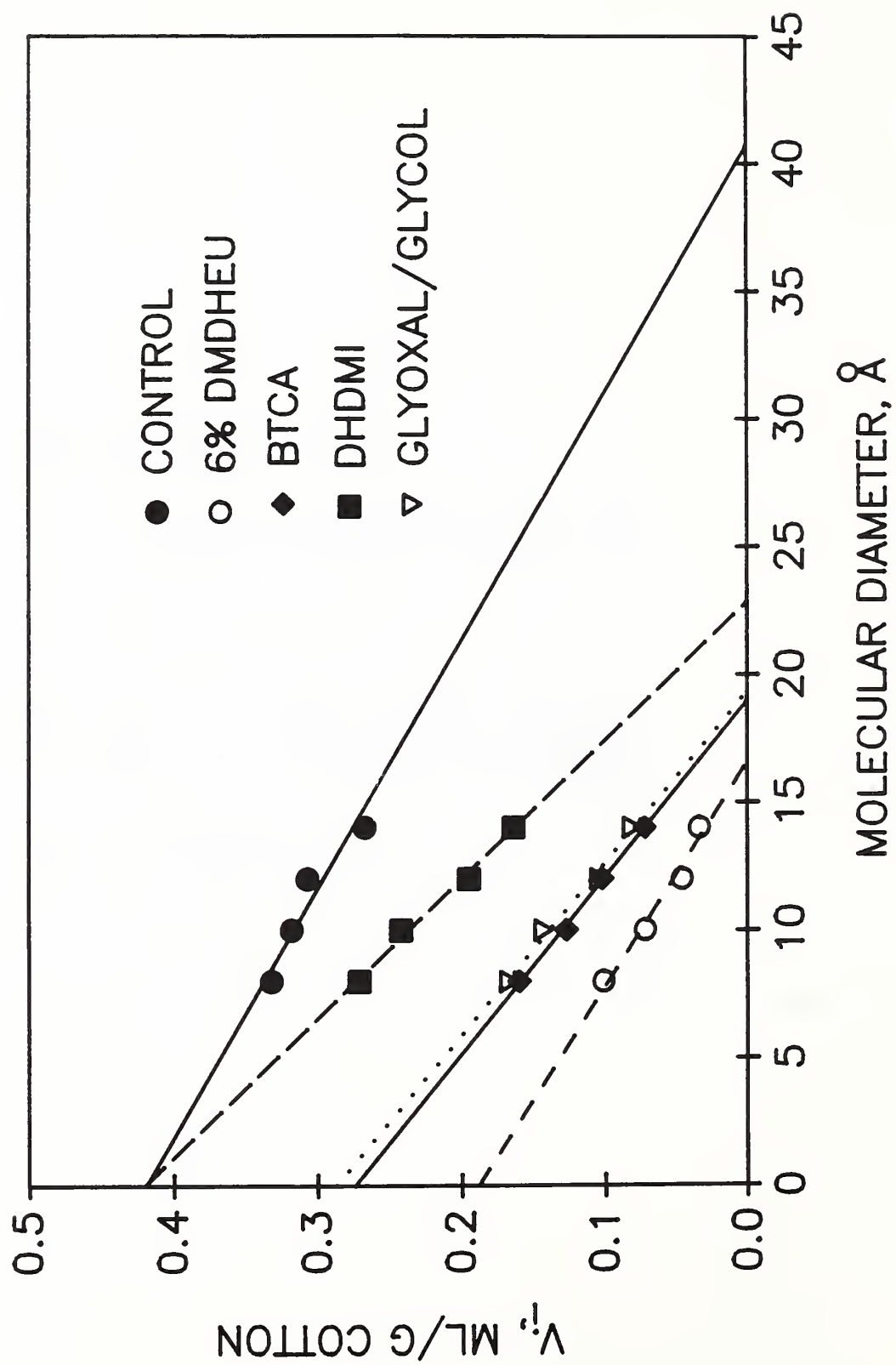
Internal volume (ml/g) accessible to molecules with molecular diameter of:

V_2 2 Å

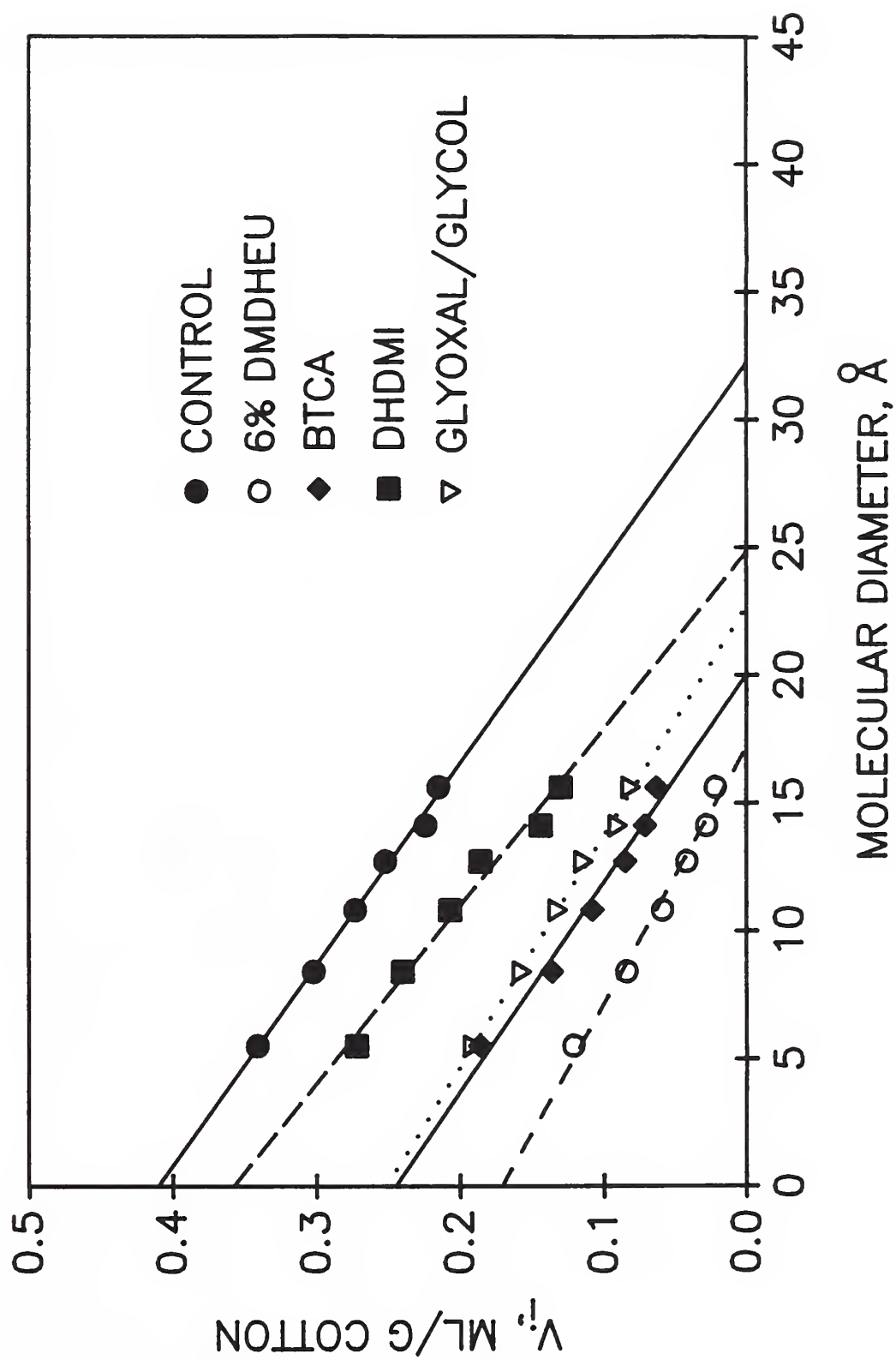
Size (Å) of the smallest molecule that is totally excluded from the internal pores of the cotton fiber.

M_x Permeability Limit

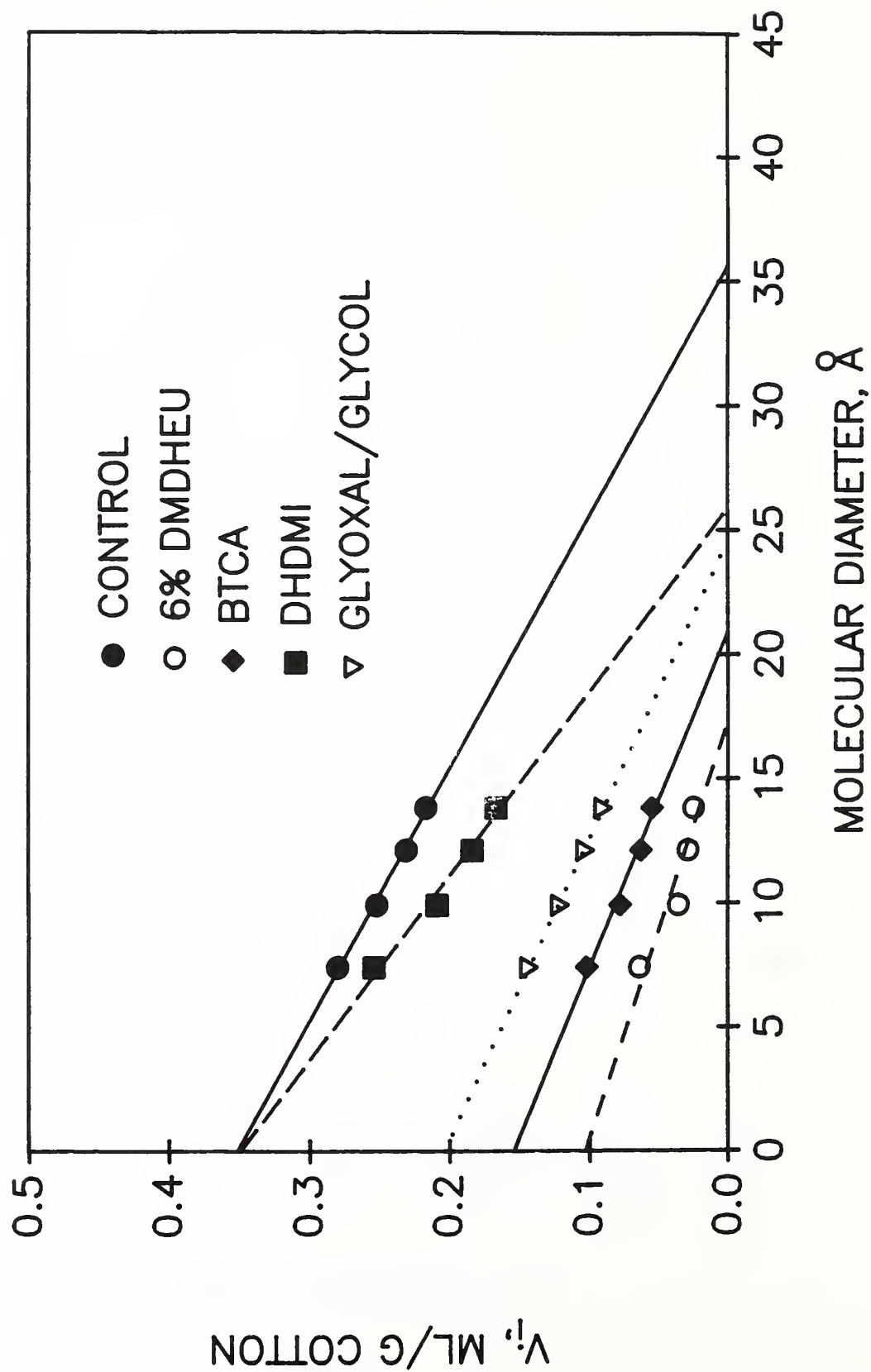
SUGARS



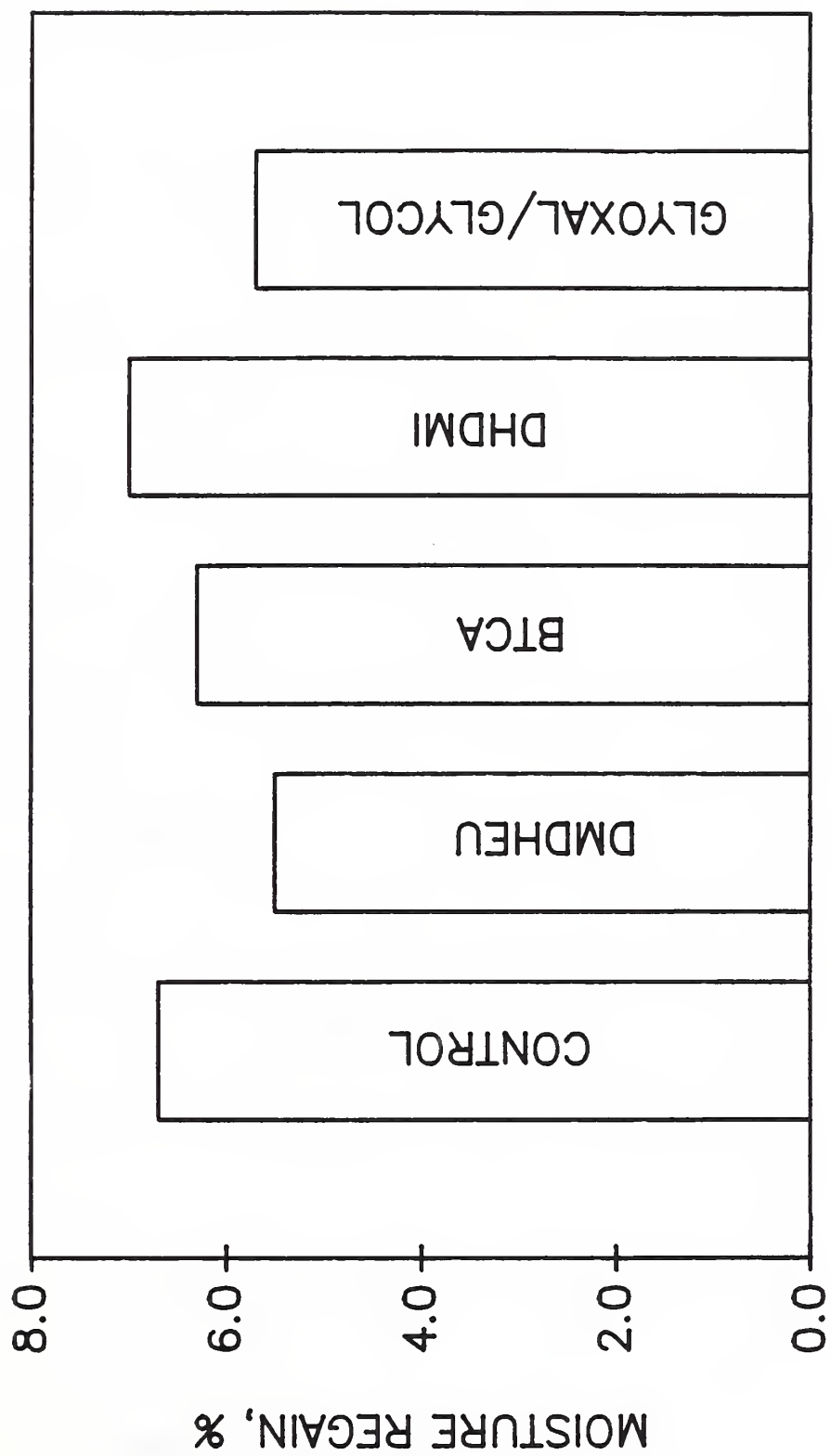
ETHYLENE GLYCOLS

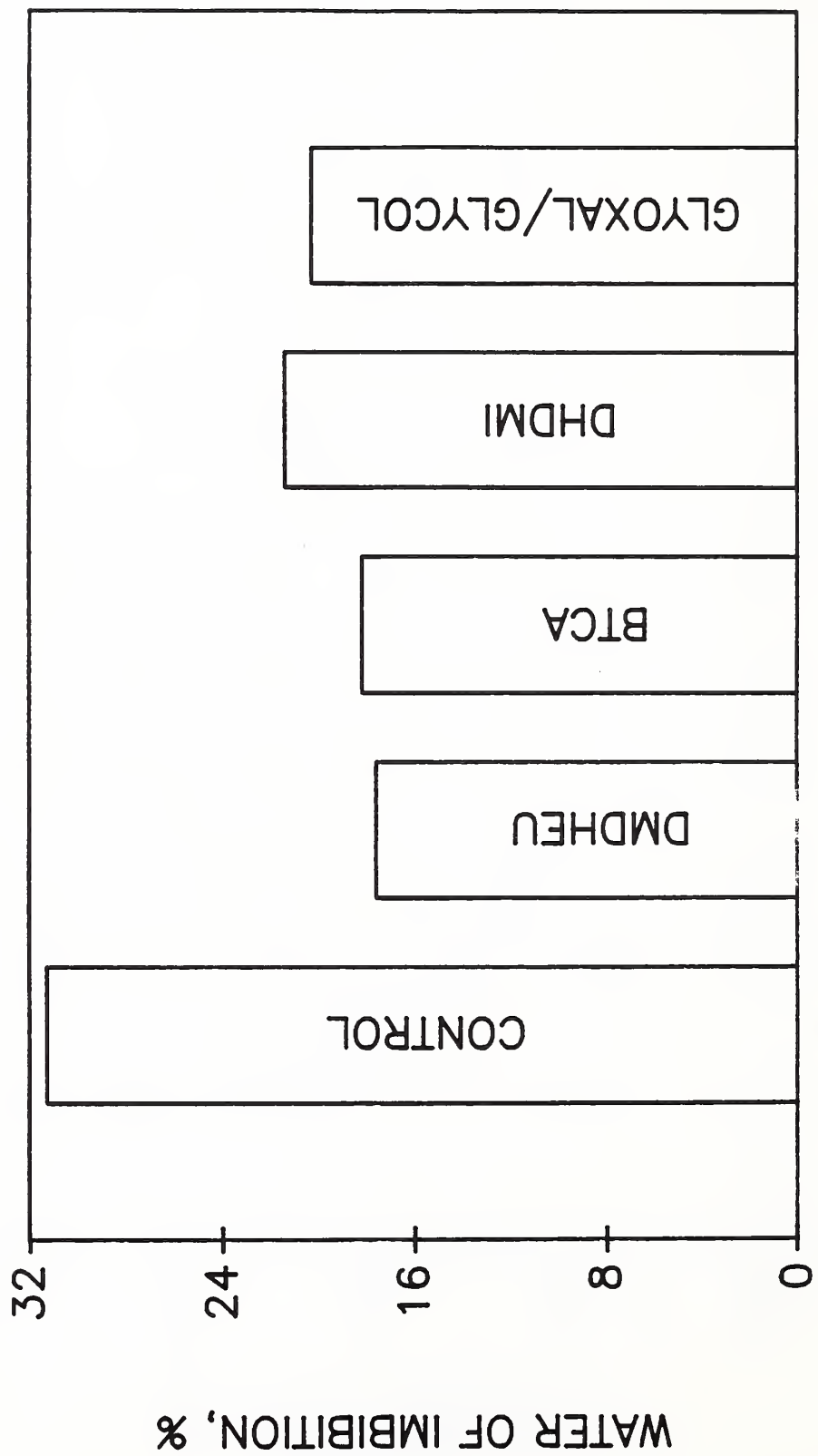


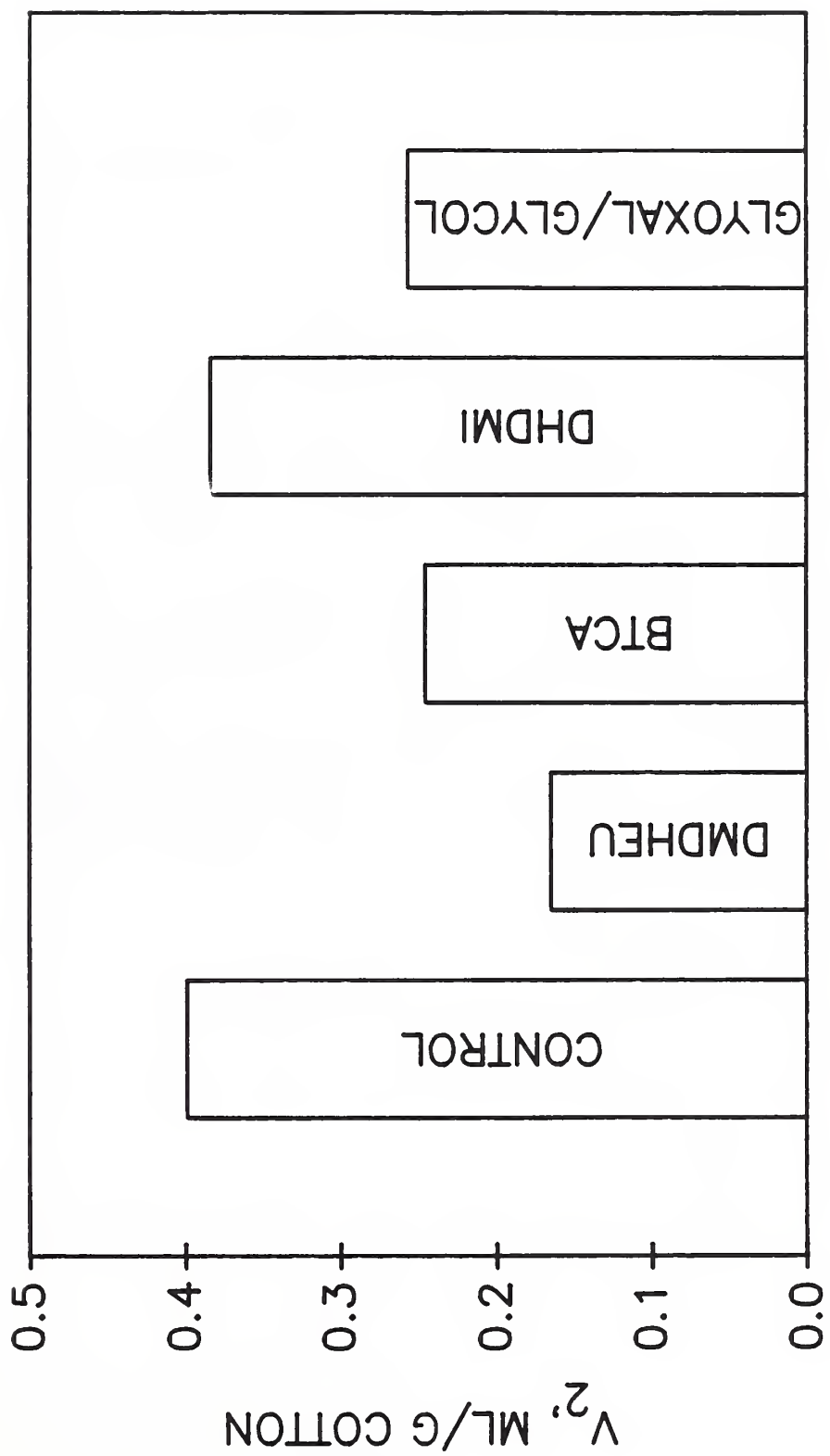
GLYMES

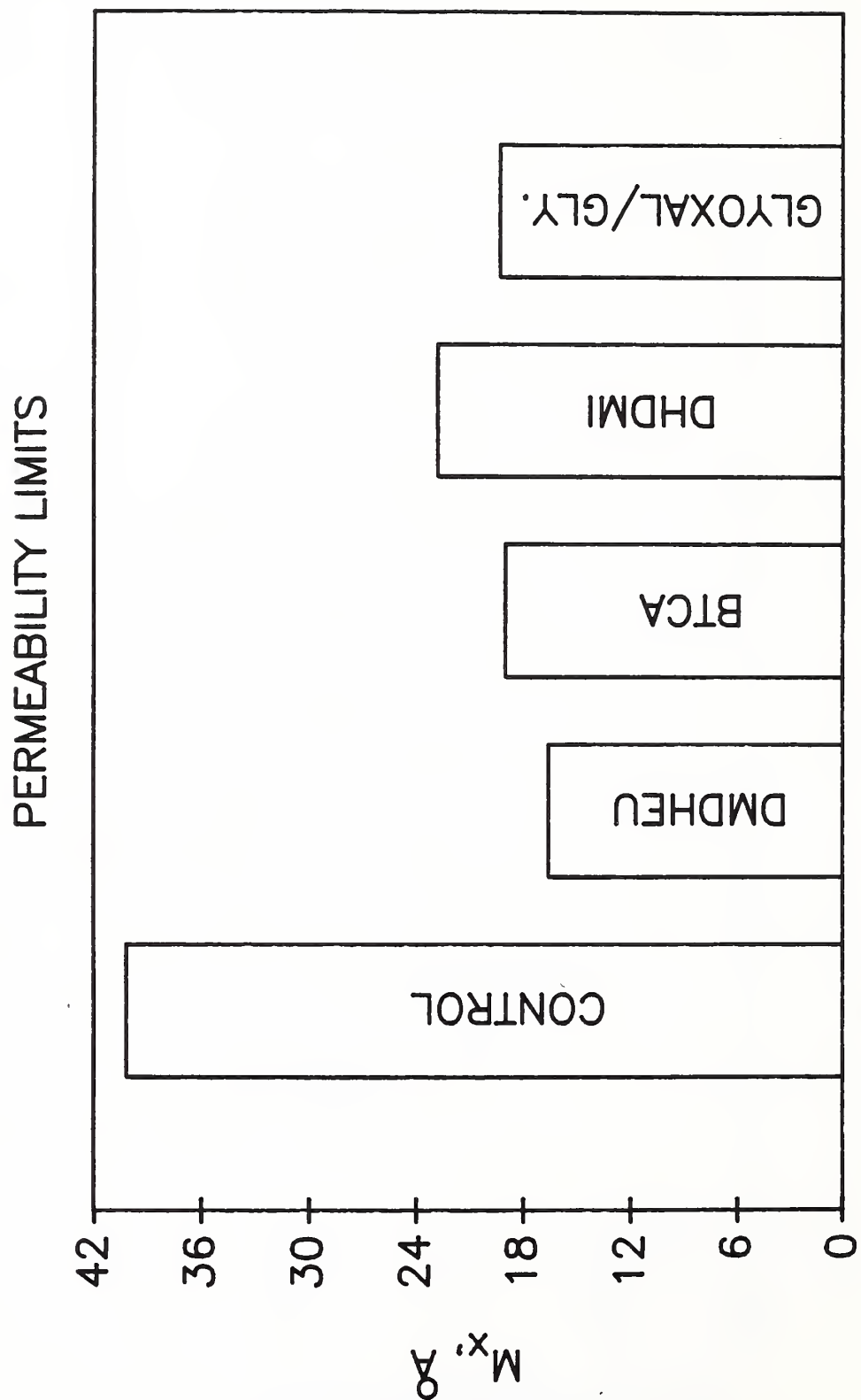


V₁, ML/G COTTON









M_x, A

SUMMARY

Comparable conditioned WRA's were realized with DMDHEU, BTCA and glyoxal/glycol; a lower value was obtained with DHDMI.

The DMDHEU-treated fabric had the highest wet WRA; comparable values were realized with the three non-formaldehyde reagents.

Retention of breaking and tearing strengths and Stoll flex abrasion resistance were highest for BTCA and DHDMI; the latter, however, had a lower level of resilience.

SUMMARY

(continued 2)

Crosslinking with DHDMI effected the lowest degree of collapse of the internal fiber volume; again this sample had a lower level of resilience.

Crosslinking with DMDHEU effected the highest degree of collapse of the internal fiber volume; this samples had the highest wet WRA.

Degree of collapse of the internal fiber volume on crosslinking with BTCA and glyoxal/glycol were comparable with less collapse observed for BTCA.

SUMMARY
(continued 3)

Moisture regain, an indication of internal surface in a conditioned state, decreased in the order control > DHDMI > BTCA > glyoxal/glycol > DMDHEU.

Water of imbibition, an indication of internal volume in the water swollen state, decreased in the order control > DHDMI > glyoxal/glycol > BTCA > DMDHEU.

SUMMARY

(continued 4)

V_2 (sugars), a measure of accessible (to molecular diameter = 2A) internal volume in the water swollen state, decreased in the order control > DHDMI > glyoxal/glycol > BTCA >> DMDHEU.

The permeability limit, i.e., the size of the smallest molecule that is totally excluded from the fiber pores, decreased in the order control >> DHDMI > BTCA > glyoxal/glycol > DMDHEU.

CONCLUSION

Formaldehyde-free crosslinking reagents effect a lower level of collapse of the internal pore structure of the cotton fiber than does DMDHEU at generally comparable levels of resilience.

Post Dyeing of Formaldehyde-Free Ester Crosslinked Cotton Fabrics

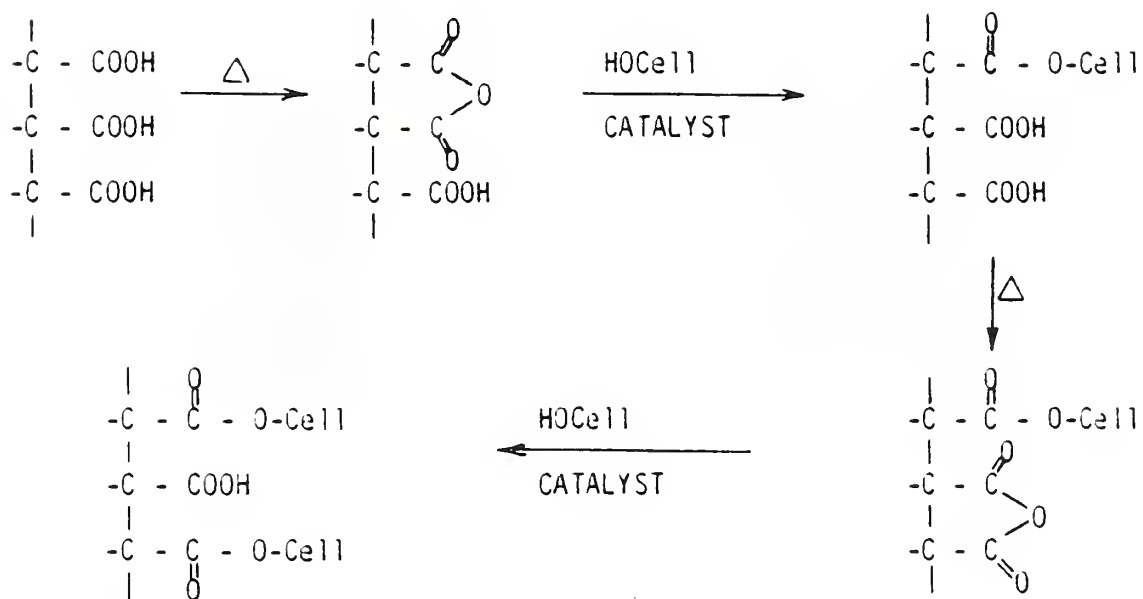
B. A. Kottes Andrews, Eugene J. Blanchard,
and Robert M. Reinhardt

Polycarboxylic acids recently have evoked widespread interest in the textile industry for durable press finishing of cotton fabrics. Major advantages are a high level of appearance properties with relatively high strength retention and the absence of formaldehyde, a subject of regulatory activity. Another potential advantage of the carboxylic acid-finished cottons is their use in the production of dyeable smooth drying fabrics. The presence of free carboxyl groups in the durable press finish can provide receptor sites for basic dyes.

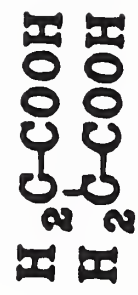
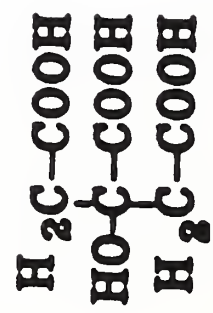
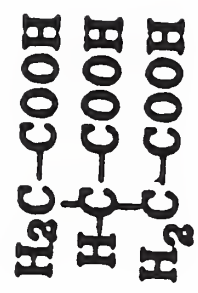
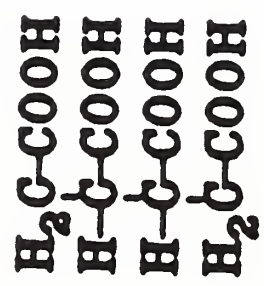
In this study the affinity of di- tri- and tetra-carboxylic acid treated cotton fabric for several basic dyes was examined. Dye receptivity was assessed by K/S, the ratio of the absorption coefficient to the scattering coefficient derived from the Kubelka-Munk equation. Unlike direct dye receptivity, depth of shade of basic dyed fabrics increased with increasing add-on of polycarboxylic acid. There was no loss of appearance properties as a result of the dyeings. However, a leveling-off of dye receptivity could be seen at higher acid add-ons.

The influence of carboxylic acid type on subsequent dyeability with these dyes was discussed. Depth of shade increased as polycarboxylic acid was varied from succinic (S) to citric (CA) to butane tetracarboxylic (BTCA) to propane tricarboxylic acid (PTCA), and as catalyst was varied from disodium phosphate (D) to monosodium phosphate (M) to sodium hypophosphite (H). Dye whiteness to laundering also followed these patterns. Basic dye concentration during dyeing of cotton finished with 6.3% BTCA and sodium hypophosphite catalyst was directly proportional to K/S value of the dyed fabric.

FORMATION OF ESTER CROSSLINKS IN COTTON

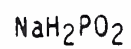
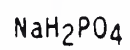
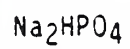


SLIDE 1



SLIDE 2

ESTERIFICATION CATALYSTS



SLIDE 3

<u>BASIC DYES</u>	<u>WAVE LENGTH OF MAXIMUM ABSORBANCE (nm)</u>
BASIC BLUE 78	600
BASIC BLUE 54	580
BASIC RED 22	540
BASIC RED 29	500
BASIC YELLOW 53	420

SLIDE 4

BASIC DYE PROCEDURE

3% DYE, owf

10% Na₂SO₄, owf

1% TRITON X-100, owf

BUFFER (FINAL pH = 4.4-4.8)

1.5% NaOAc, owf

1.5% HOAc, owf

AHIBA POLYMAT DYEING MACHINE

60 MIN, 95°C

15 MIN COOL DOWN TO 60°C

15 MIN RINSE, RUNNING TAP WATER

SLIDE 5

DIRECT DYES

MOL WT

DIRECT RED 81

630

DIRECT RED 79

1050

DIRECT RED 80

1250

SLIDE 6

DIRECT DYE PROCEDURE

3% DYE, owf

20% NaCl, owf

1% TRITON X-100, owf

pH = 3

AHIBA POLYMAT DYEING MACHINE

60 MIN, 95°C

15 MIN COOL DOWN TO 60°C

15 MIN RINSE, RUNNING TAP WATER

SLIDE 7

ACID	% UNTREATED K/S		
	DIRECT RED 81 (630)*	DIRECT RED 79 (1050)	DIRECT RED 80 (1250)
BTCA	5.3	3.1	1.4
PTCA	7.6	3.6	1.4
CA	17.7	5.5	3.0
SA	42.0	25.5	20.4

*NUMBERS IN PARENTHESES ARE MOLECULAR WEIGHTS OF THE DYES.

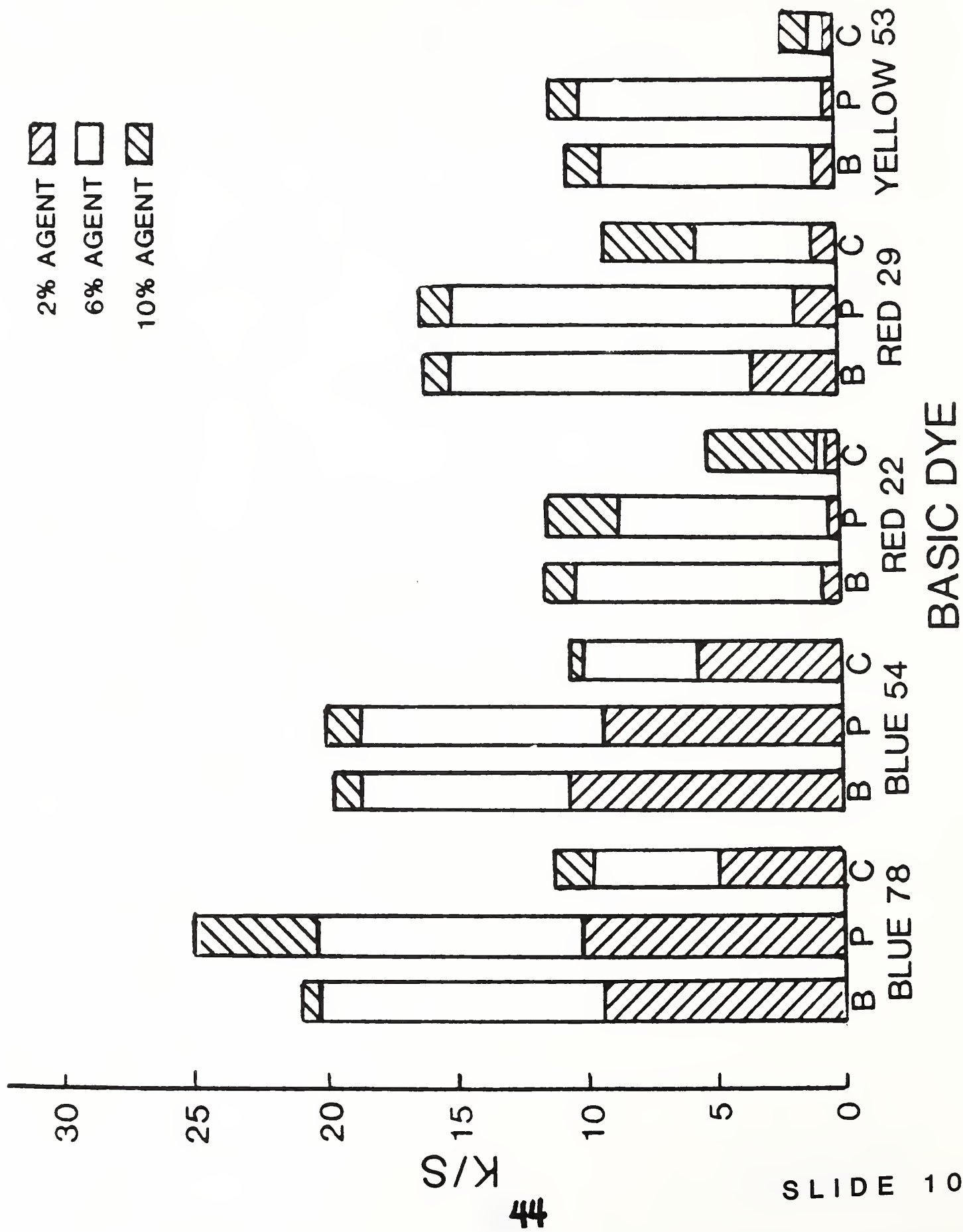
SLIDE 8

FABRIC PROPERTIES AFTER DYEING WITH BASIC BLUE 78

ACID	DP RATING AFTER RINSE	BREAKING STRENGTH LB, W	K/S AFTER RINSE
BTCA	4.0 (4.5)*	29 (24)	19.3
PTCA	3.7 (4.3)	30 (29)	22.4
CA	3.5 (3.8)	24 (27)	12.3
SA	2.7 (2.8)	26 (30)	12.0
UNTREATED	1.5	51	2.1

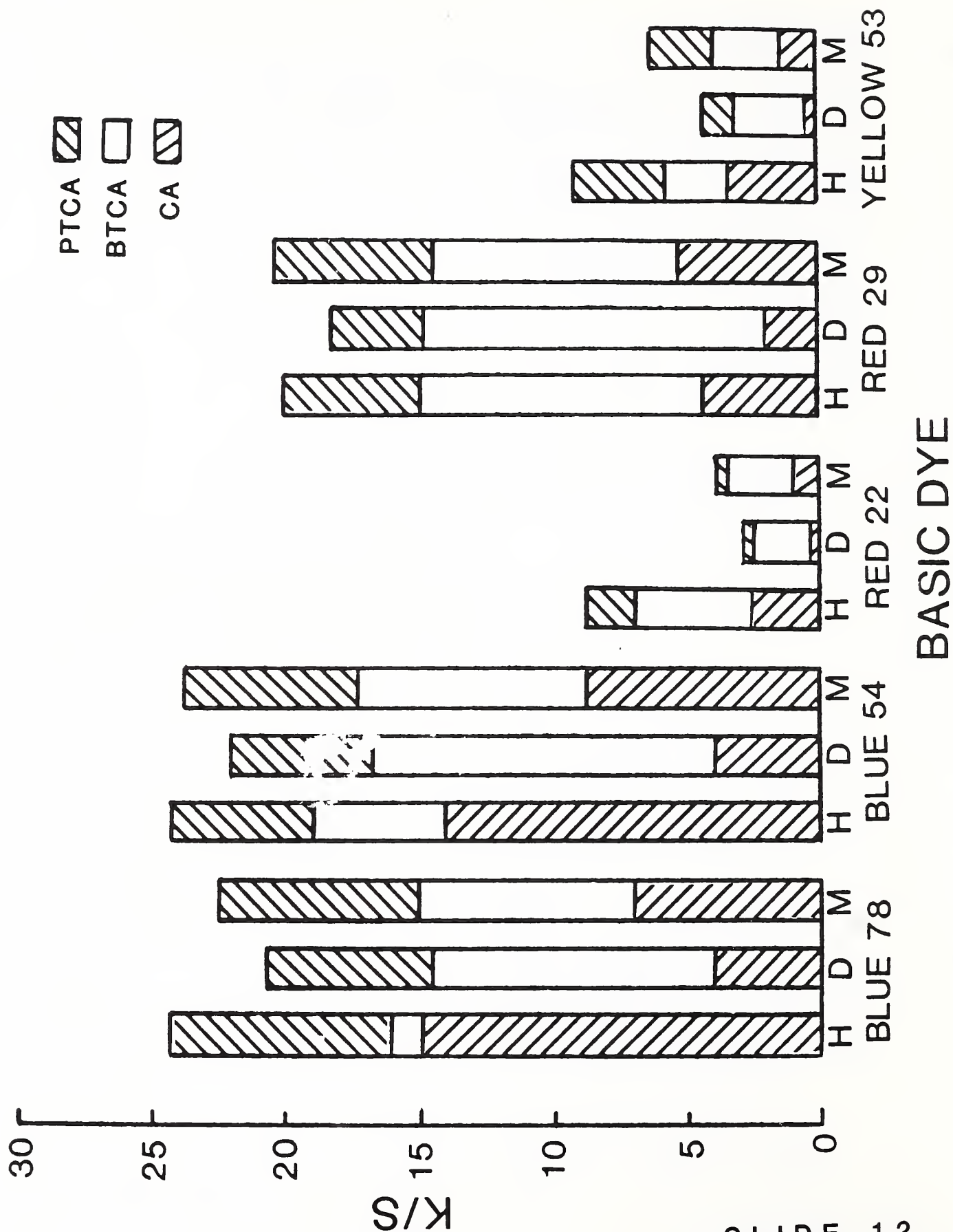
* NUMBERS IN PARENTHESES DENOTE VALUES OF FABRICS BEFORE DYEING

SLIDE 9



DYE	% RINSED K/S AFTER 1 LAUNDERING								
	BTCA			PTCA			CA		
	2	6	10	2	6	10	2	6	10
BASIC BLUE 78	33	60	74	20	54	77	17	28	32
BASIC BLUE 54	41	56	68	36	66	60	31	42	45
BASIC RED 22	7	12	19	--	5	33	--	4	8
BASIC RED 29	17	55	62	11	41	77	10	26	23
BASIC YELLOW 53	5	30	32	--	12	18	--	10	9

SLIDE 11

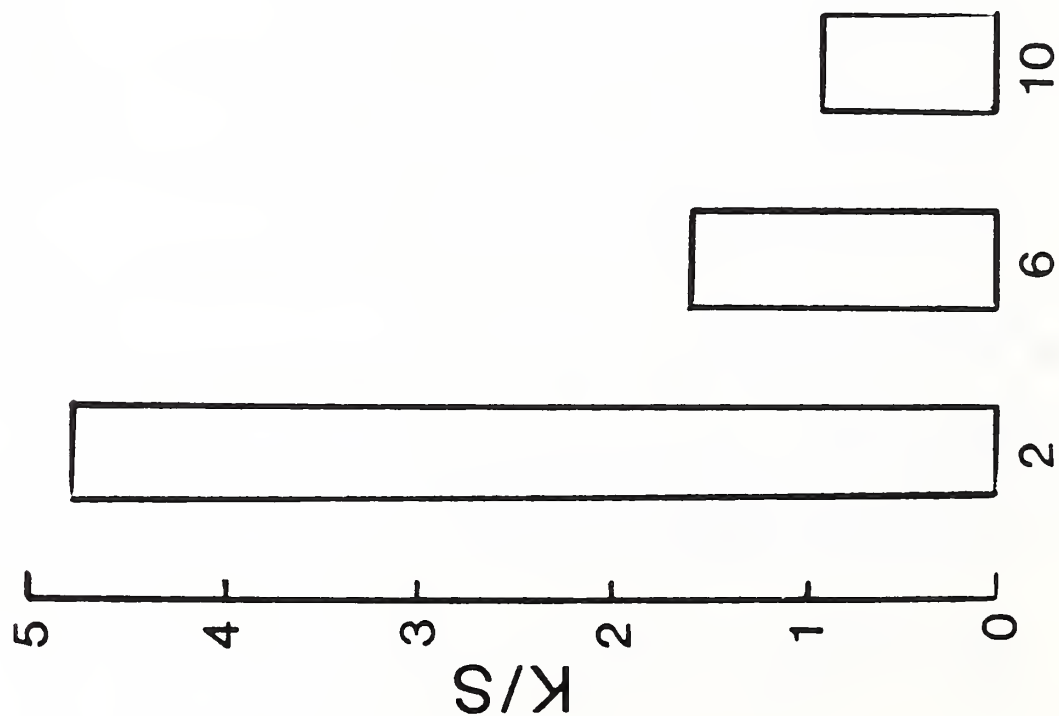


DYE	% RINSED K/S AFTER 1 LAUNDERING								
	NaH_2PO_2			Na_2HPO_4			NaH_2PO_4		
	B*	P	C	B	P	C	B	P	C
BASIC BLUE 78	68	77	38	64	53	20	73	38	31
BASIC BLUE 54	58	60	40	59	48	37	58	55	40
BASIC RED 22	62	42	8	15	7	--	11	11	10
BASIC RED 29	60	63	27	41	30	9	30	45	11
BASIC YELLOW 53	67	61	12	28	--	--	32	7	14

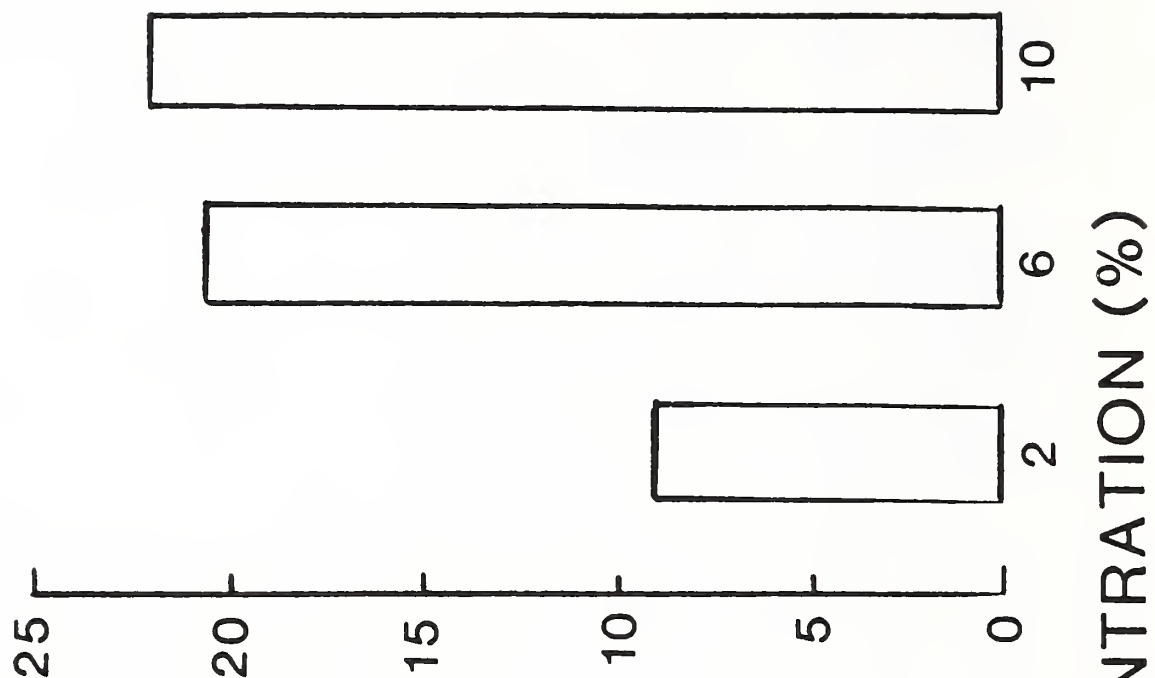
*B = BTCA; P = PTCA; C = CA.

SLIDE 13

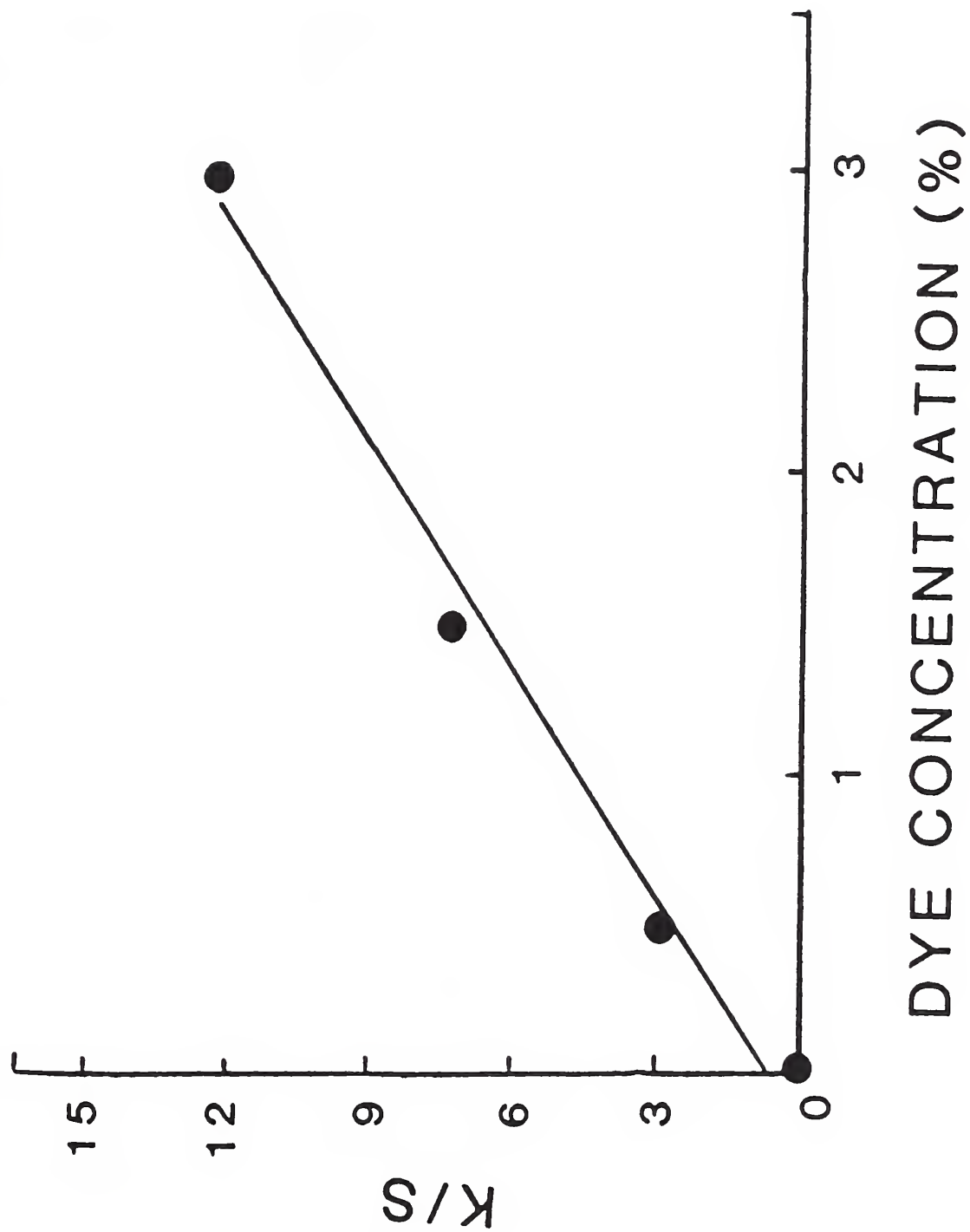
DIRECT RED 81



BASIC BLUE 78



BTCA FINISH, BASIC BLUE 78



SUMMARY

- * FREE CARBOXYL GROUPS IN POLYCARBOXYLIC ACID-FINISHED FABRICS PROVIDE SITES FOR BASIC DYE ATTACHMENT
- * OF BTCA, PTCA, CA AND SA, BTCA AND PTCA ARE THE MOST RECEPTIVE TO BASIC DYES
- * DYEABILITY INCREASES WITH INCREASING ADD-ON OF ACID, BUT APPEARS TO REACH A SATURATION MAXIMUM
- * CATALYSTS INFLUENCE DYEABILITY: $\text{NaH}_2\text{PO}_2 > \text{NaH}_2\text{PO}_4 > \text{Na}_2\text{HPO}_4$
- * ESTER CROSSLINKED FABRICS CAN PROVIDE A ROUTE TO FORMALDEHYDE-FREE DURABLE PRESS DYEABLE FABRIC

SLIDE 16

THERMAL DECOMPOSITION OF POLYCARBOXYLIC ACIDS

BRENDA J. MORRELL AND B. A. K. ANDREWS

For years durable press properties have been achieved for cotton fabrics by reaction with agents based upon cyclic ureas. Such finishes have excellent smooth drying properties and are durable to repeated laundering. These finishes have disadvantages that include lower fabric strength and some finish hydrolysis with the subsequent liberation of formaldehyde.¹ Recently, there has been renewed interest in the use of carboxylic acids for production of smooth drying cotton fabrics. With a new class of catalysts based on phosphorus-containing inorganic acids, durable press (DP) levels of appearance properties have been achieved. The polycarboxylic acids (PCA) offer the same advantages as those mentioned above. In addition, they cause somewhat less strength loss and release no formaldehyde.

To achieve smooth drying properties with fabrics of cotton cellulosics, chemical crosslinks are necessary throughout the entire fiber matrix. Traditionally, finishes achieved crosslinks through etherification of the cellulose. Reaction of cellulose with the carboxylic acids is achieved by esterification. The proposed mechanism for this reaction involves formation of an anhydride intermediate which subsequently reacts with a cellulose hydroxyl group. A single pendant carboxylic acid group is reformed. Dicarboxylic acids can form only one anhydride, therefore no further reaction with cellulose is likely and few if any crosslinks are achieved. Of interest to the textile industry are those acids with three or more carboxylic acid groups so that formation of at least a second anhydride is theoretically possible. Such compounds would be capable of crosslinking cellulose. To date the best fabric performance has been achieved with a tetracarboxylic acid: 1,2,3,4-butanetetracarboxylic acid (BTCA). The agent cost is high; however, the industry interest is so strong that efforts to produce the agent more economically are underway.

As research on finishes from these polycarboxylic acids has progressed, we began a complementary study on the thermal characteristics of the same compounds. Ten di- tri- and tetra-functional, polycarboxylic acids were examined with three thermoanalytical techniques. Thermograms produced at 600 °C agreed well with melting point data and, when combined with the peak temperatures and profiles, could be used to distinguish among the compounds. Thermal parameters were found useful in describing fundamental relationships among the samples as well as providing practical information of interest to the textile industry. For example, total heats of reactions generally

increased as the number of functional groups increased. In addition, the polycarboxylic acids with the olefinic linkages had smaller total heat values than did their corresponding hydroxyl-substituted acids.

When percent residue values at simulated cure temperatures were analyzed along with the corresponding rates of weight-loss, we were able to make a preliminary assessment of a compound's potential usefulness as a textile finishing agent. Due to the excessive and rapid weight-loss by maleic acid under thermal stress, this compound would be the least likely to perform well as a cellulose DP reagent. However, these same properties appear to be better balanced with the tetra-functional compounds, especially with all-cis-CP-TCA and BTCA.

Evidence was found to support the proposed mechanism of PCA's reaction with cellulose by way of an anhydride transition state. Thermoanalytical data indicated that water-loss occurred with the acids containing an olefinic linkage or especially with the larger compounds. Evidence of possible dianhydride formation was found with all-cis-CP-TCA and BTCA. To date, finishes from BTCA have performed best in textile finishing applications.

ACKNOWLEDGEMENT

The authors wish to thank Mary Patterson for laboratory technical assistance.

INTRODUCTION: Traditional durable press finishes for cotton fabrics provided these properties: smooth drying, lower fabric strength, and finish hydrolysis-- including release of formaldehyde

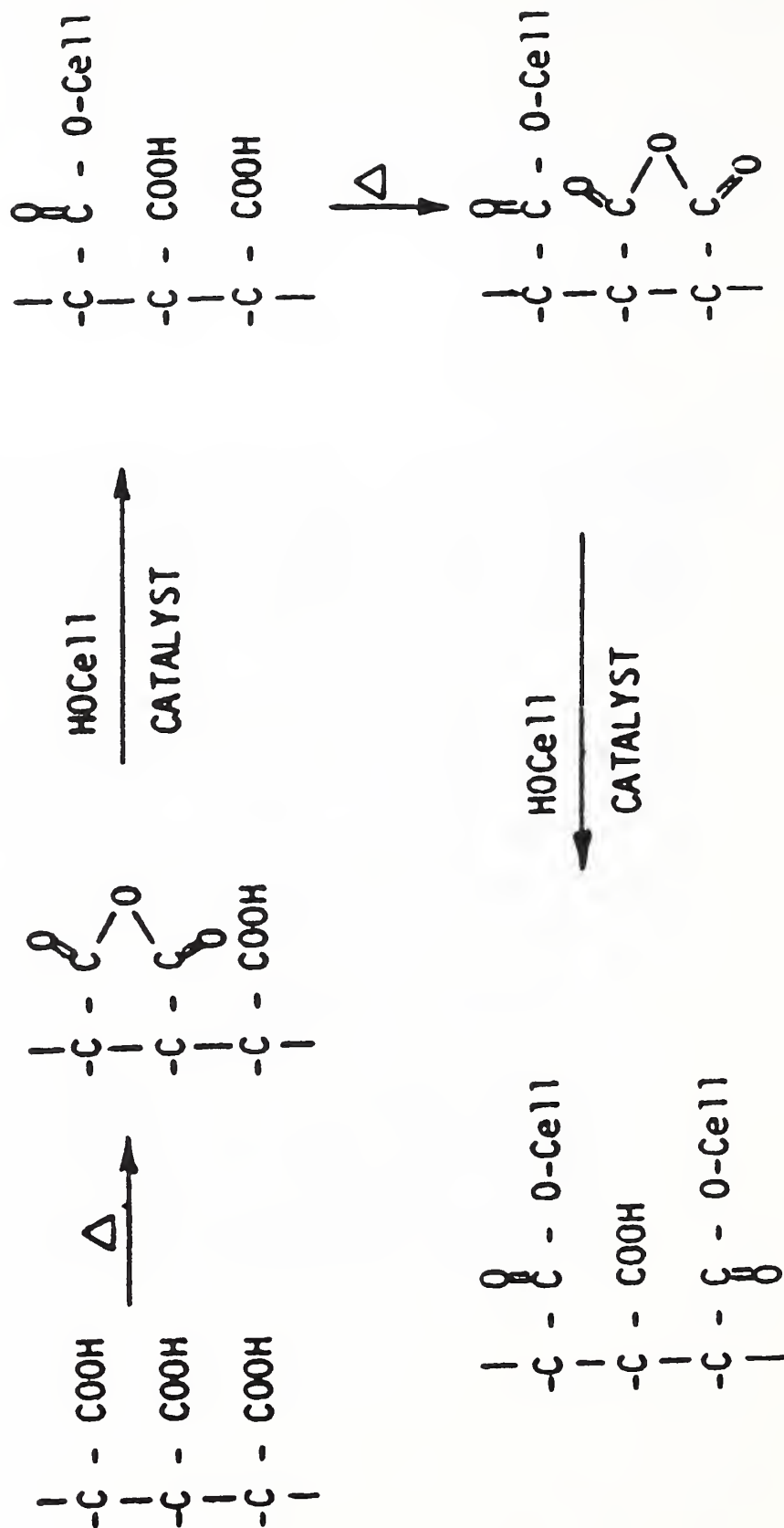
Polycarboxylic acid (PCA) finishes provide: smooth drying, somewhat higher fabric strength, and no release of formaldehyde

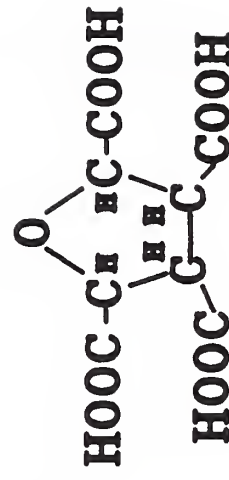
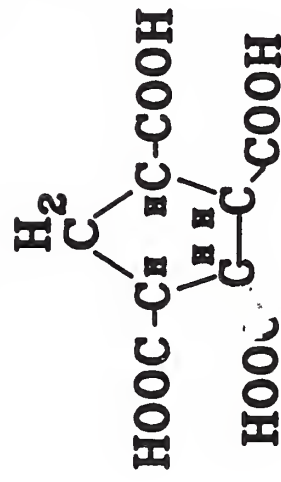
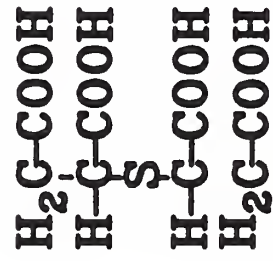
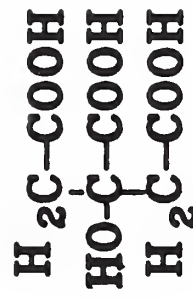
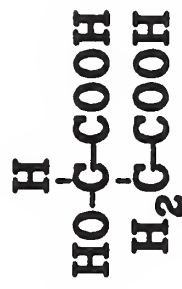
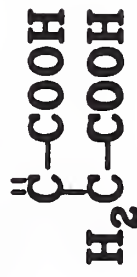
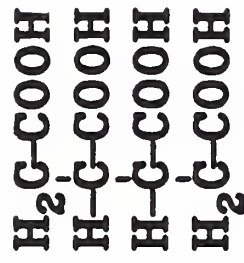
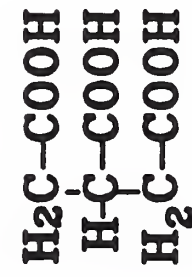
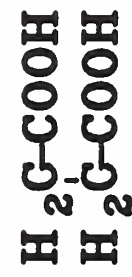
Durable press finishing requires chemical crosslinking throughout the fabric

traditional finishes -- through etherification

PCA finishes -- through esterification via a proposed mechanism of anhydride formation. Theoretically, the best crosslinking would be through dianhydride formation.

FORMATION OF ESTER CROSSLINKS IN COTTON





THERMAL ANALYTICAL TEST CONDITIONS

DSC **DIFFERENTIAL SCANNING CALORIMETRIC**

TG **THERMOGRAVIMETRIC**

DTG **DIFFERENTIAL THERMOGRAVIMETRIC**

SIMULATED CURE CONDITIONS

held 1 min at 60°C

heated at 25°C/min to maximum
(180 or 160°C)

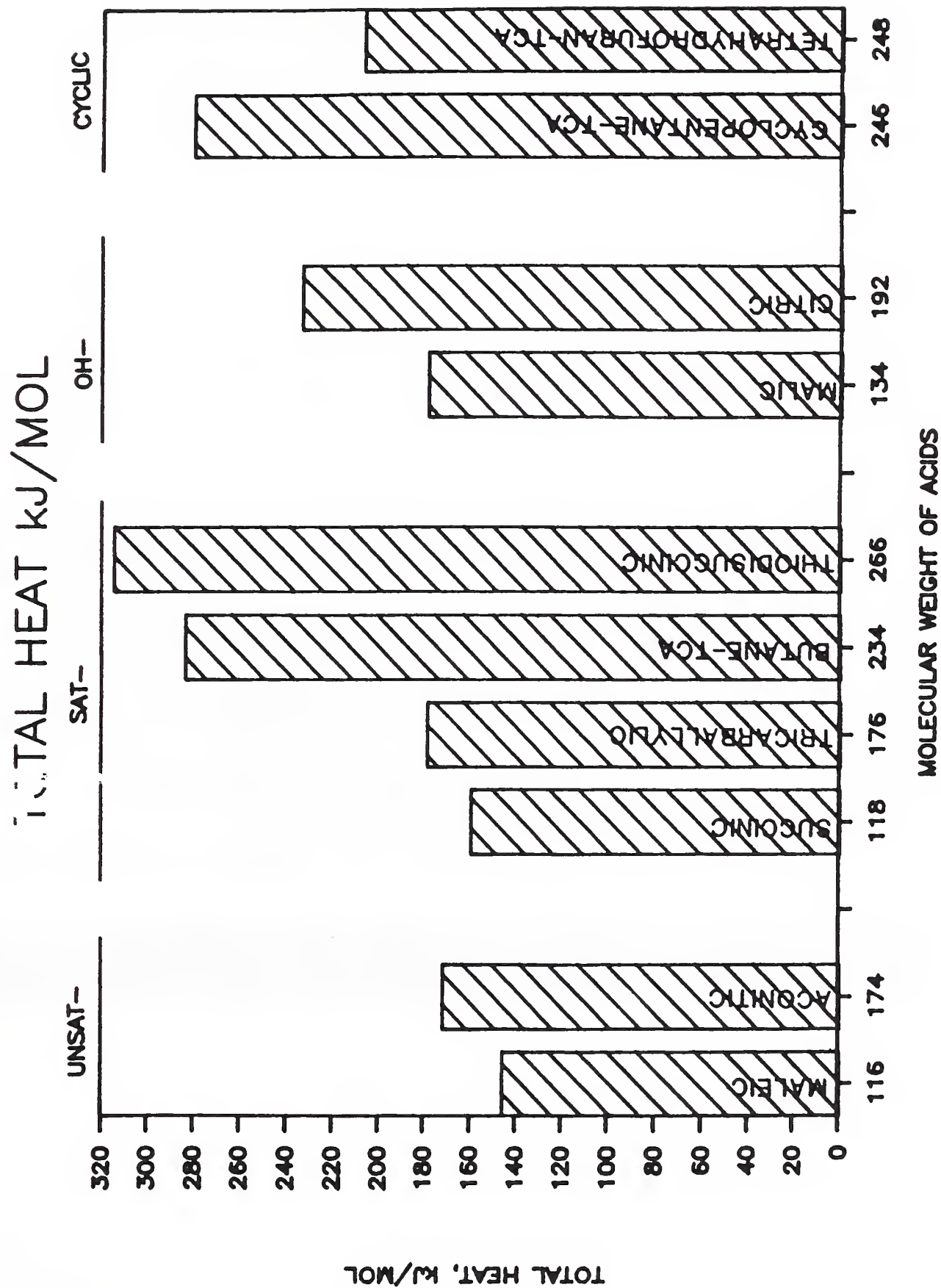
held 3 min at maximum

GENERAL THERMAL CONDITIONS

heated from ambient to 600°C
at 15°C/min

Total Heats of Reaction increase in the order
DI- < TRI- < TETRA-CARBOXYLIC ACIDS
and

UNSAT. . SAT. < OH- < TETRA- CA
(maleic acid has the least thermal stability
tetra-carboxylic acids have the greatest)

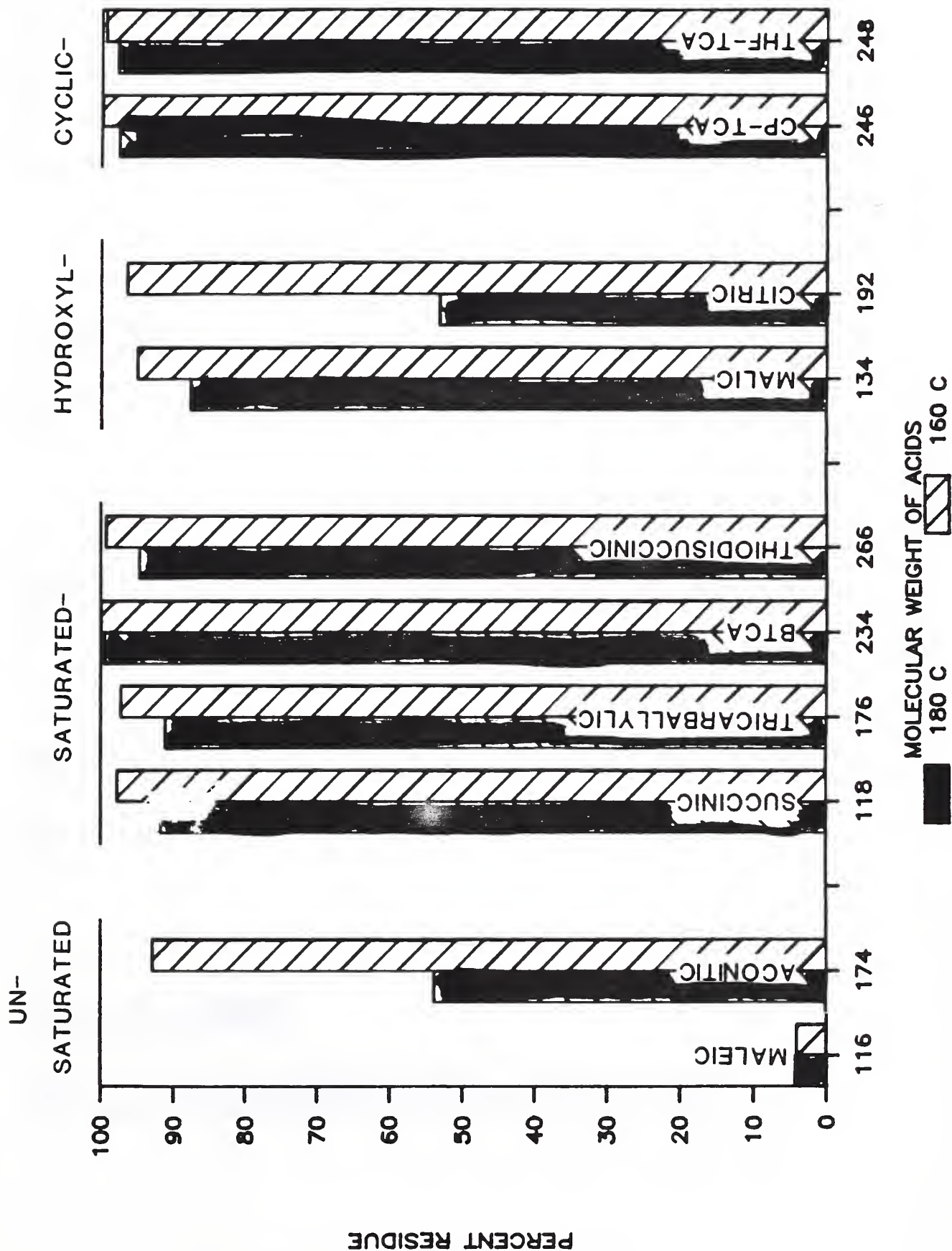


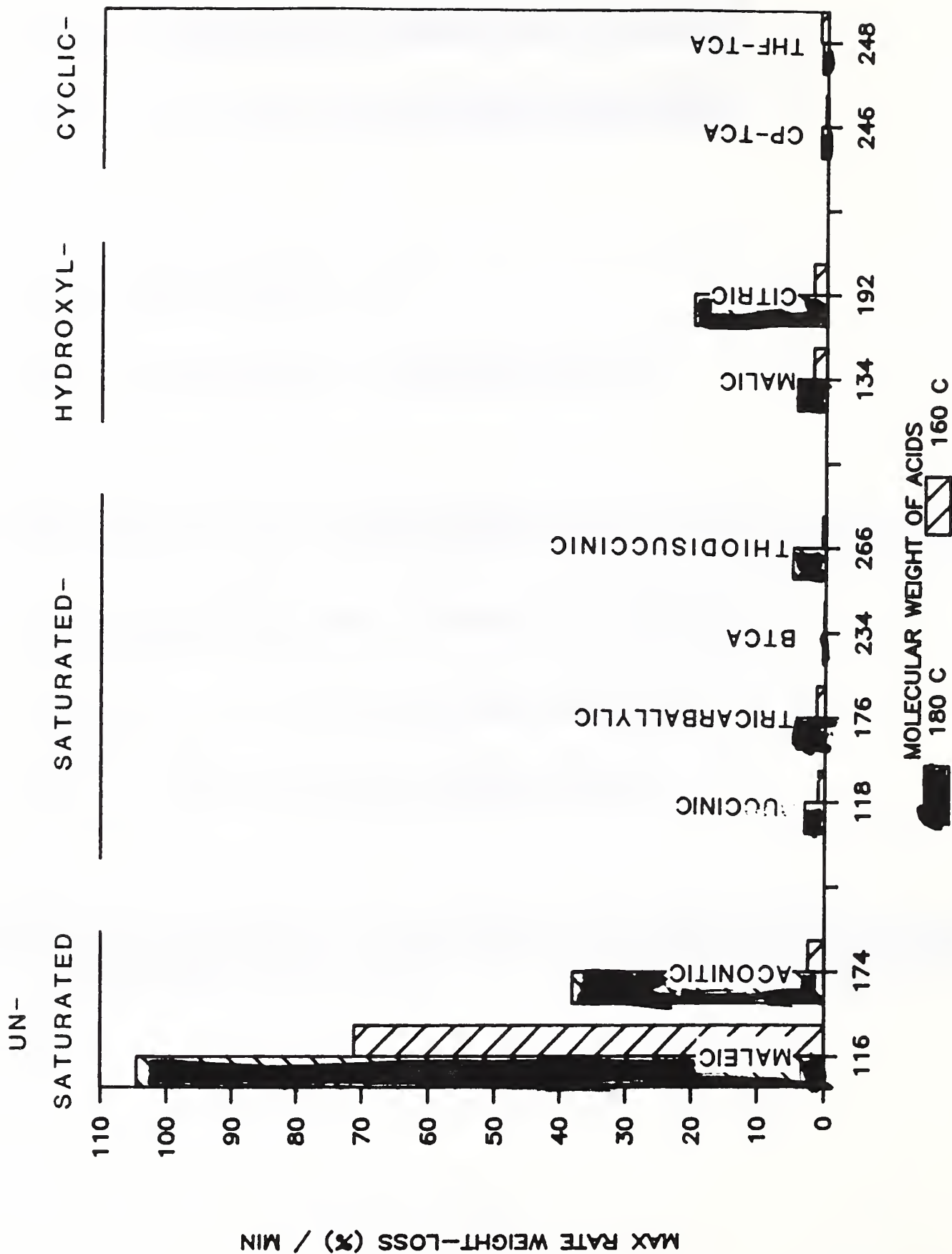
Percent residue values increase in the order

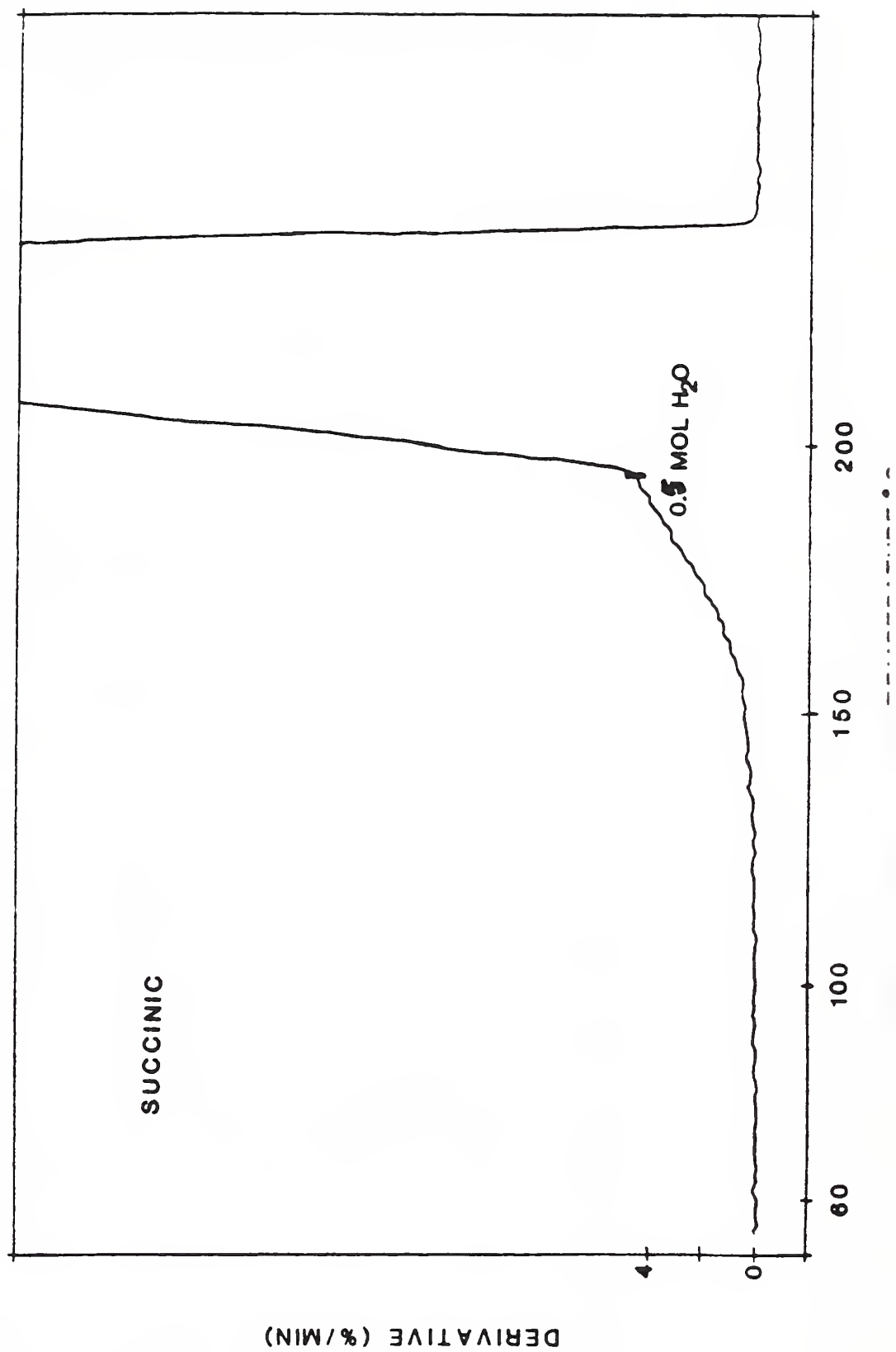
DI- < TRI- < TETRA-CARBOXYLIC ACIDS

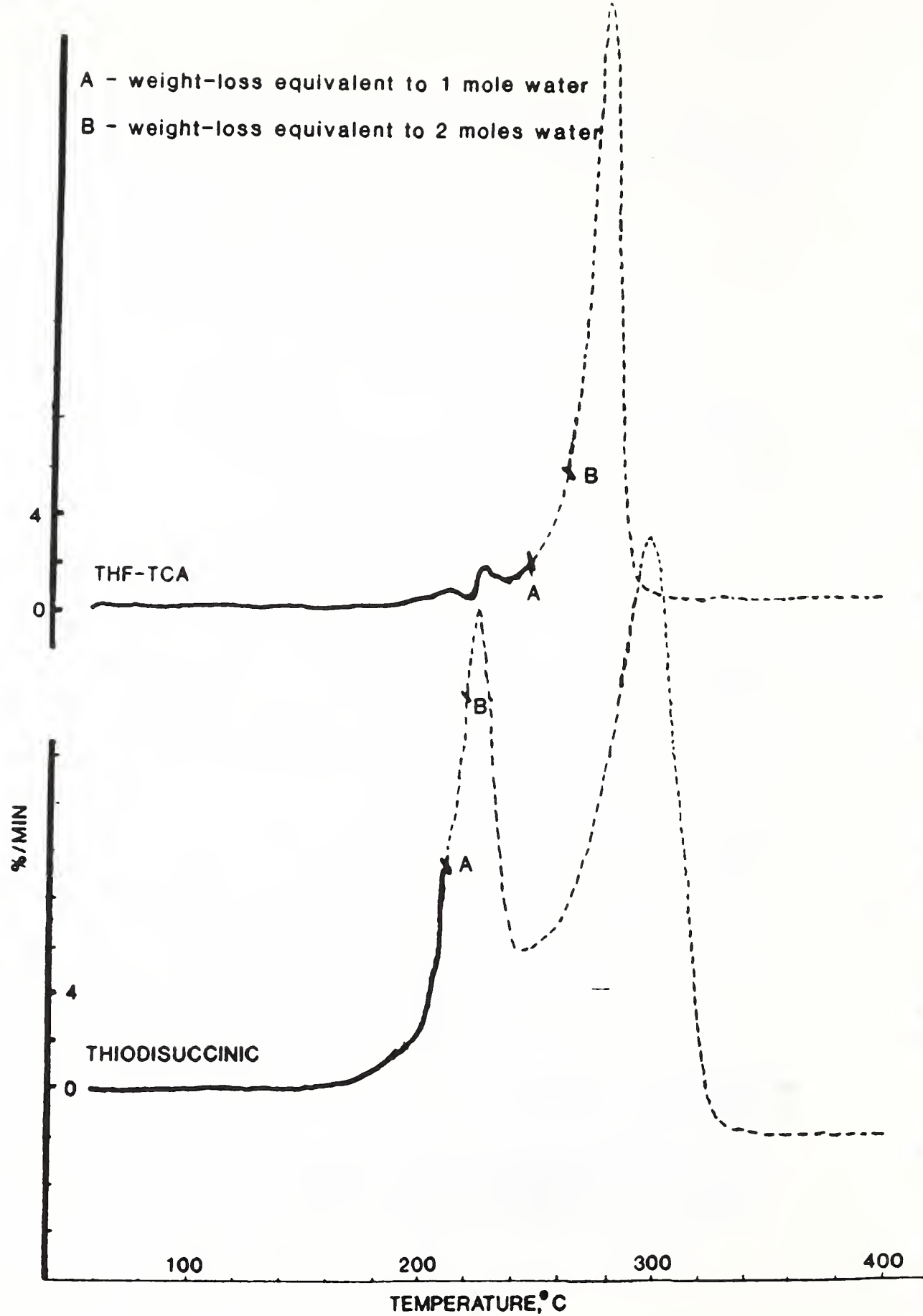
(structural relationships are absent)

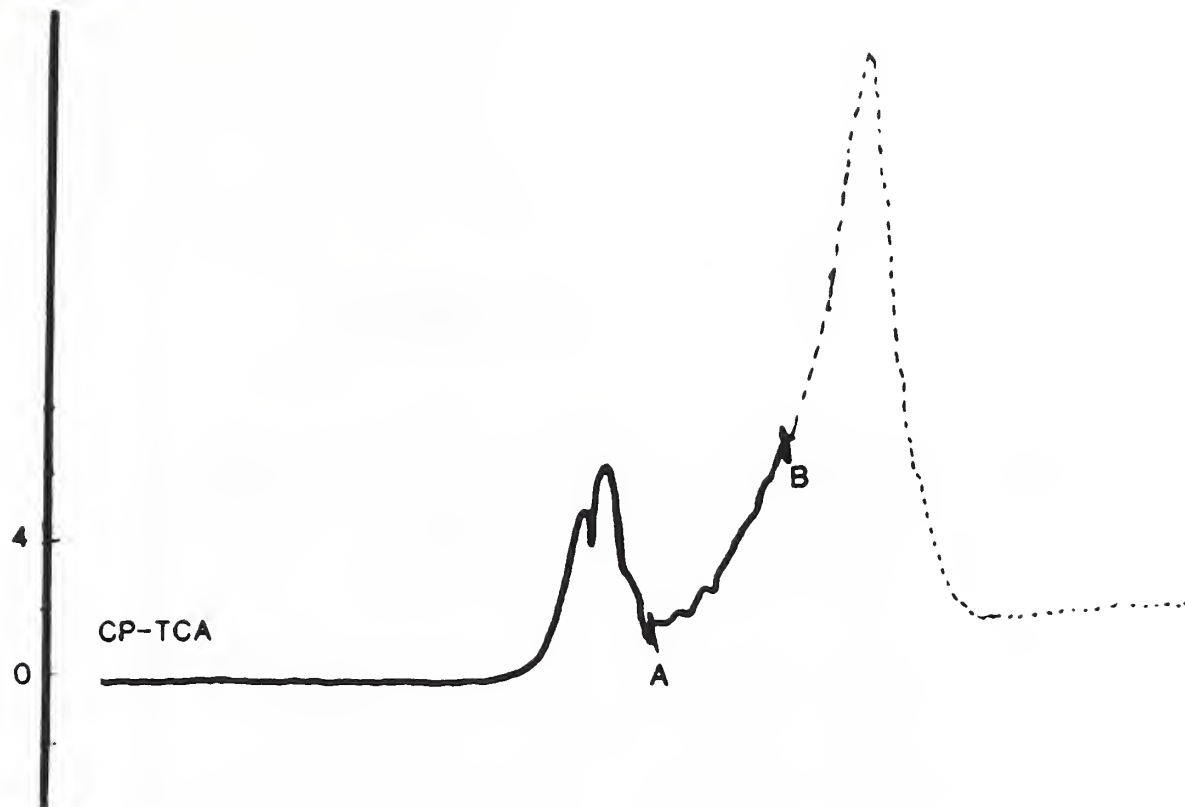
(maleic acid produced the least--least usable)





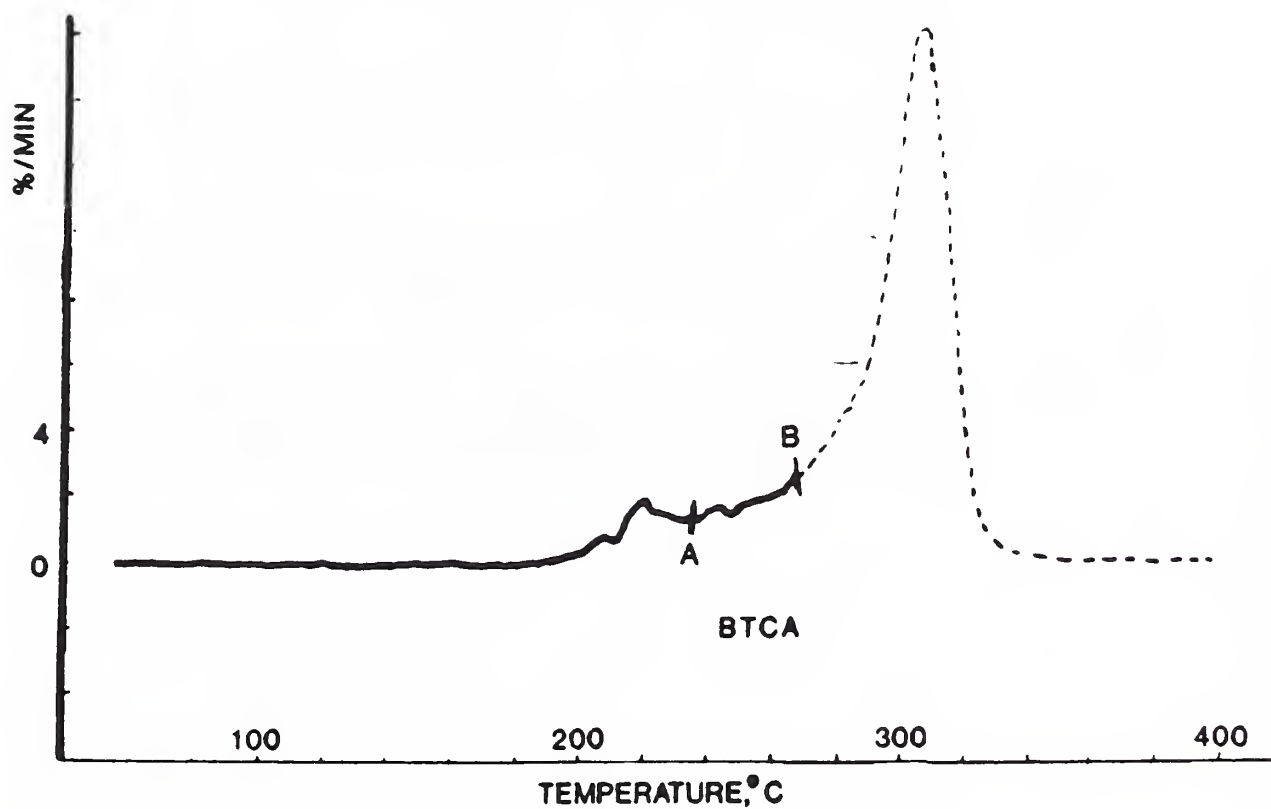






A - weight-loss equivalent to 1 mole water

B - weight-loss equivalent to 2 moles water



SUMMARY

- I. Used thermoanalytical techniques to study PCA's
Could distinguish among 10 compounds
- II. Total heats of reaction data were used to classify
compounds' thermal stability
Tetracarboxylic acids were the most stable
- III. Percent residue data, especially at simulated cure
temperature indicated potential usefulness as a
textile finishing agent
Tetracarboxylic acids were better; CP-TCA and
BTCA were best
- IV. Provided support for the esterification mechanism
via anhydride formation
- V. Increased knowledge of PCA's and their potential
as Durable Press reactants for cotton textiles

Catalysts for the High Speed Esterification
and
Crosslinking of Cotton by Polycarboxylic Acids

Clark M. Welch

Recent work at SRRC has shown that polycarboxylic acids are a promising class of durable press (DP) finishing agents for cotton. In the presence of heat and catalyst they crosslink the cotton cellulose through esterification of cellulosic hydroxyl groups. Two of the most effective agents are shown in Fig. 1.

The way in which these agents react with cotton is probably as shown in Fig. 2. The reactive intermediates appear to be cyclic anhydrides formed by splitting off water from adjacent carboxyl groups. Even if the central carboxyl group is the one initially esterified, the resulting product will have an ester group flanked by two carboxyls which can then form a 6-membered anhydride ring and esterify a second cellulosic hydroxyl group, thus completing the crosslink.

Evidence for the anhydride mechanism of esterification is noted in Fig. 3. It is well known that weak bases do catalyze esterification of alcohols and of cellulose, by anhydrides of carboxylic acids; hence the effectiveness of such catalysts in the present processes. Moreover, if dicarboxylic acids are used, few crosslinks appear to be formed. After the first carboxyl group is esterified, the second is situated by itself and cannot form an anhydride ring required for the second esterification needed to complete the crosslink. Thermoanalytical studies of Morrell and Andrews confirm that the polycarboxylic acids used here do lose water when heated, in conformity with the anhydride theory.

The pad-dry-cure method of applying butanetetracarboxylic acid (BTCA) is shown in Fig. 4. In our earliest work, high wet pickups were used, and cure time (90 sec.) was longer than most mills would prefer to use. Sodium hypophosphite, the most active catalyst, produced the results shown in Fig. 5. A high level of DP performance was imparted with 1.6-6.5% catalyst present, and a useful level of performance was maintained for 90-100 home laundering cycles, using AATCC standard detergent 124 (a phosphate-built detergent). The samples were laundered and tumble dried as a 4lb. load in all cycles. The lot of printcloth on which the finish had the higher durability was the more absorbent, and gave higher wet pickups than the other lot. The treatment run without polyethylene also used a higher wet pickup than the other runs.

The results of curing BTCA at higher temperatures (Fig. 6) show that the curing times could be considerably shortened without much adverse effect on performance or durability of the finish. In fact the finish cured at 215°C for 15 seconds was

more durable than if cured at 180°C for 45-90 seconds. These results were obtained at high catalyst concentration.

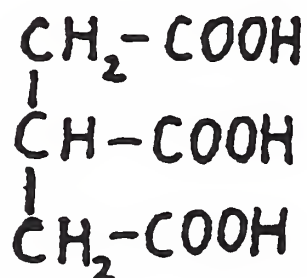
The wet pickups could be decreased, and less catalyst could readily be used, as shown in Fig. 7. A high level of DP performance could be obtained on curing at 215°C for 15-20 seconds. We did not use a preheater in these studies, and so a portion of the "cure times" (actually the residence time in the oven) was consumed in bringing the fabric from room temperature up to the actual cure temperature. Also shown in Fig. 7. is a run made with propanetricarboxylic acid. High initial performance was imparted and the laundering durability, though a little more than half that for BTCA, was ample for many possible end uses.

The physical properties of a number of runs of Fig. 7. are shown in Fig. 8. Little difference was evident in the strength properties obtained in high temperature-short time cures compared to the strength after lower temperature-longer cures.

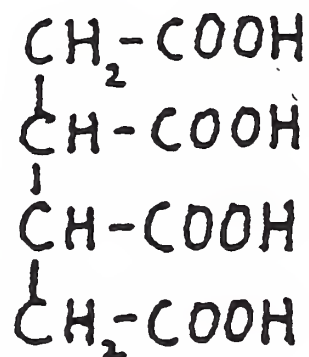
Results with mixed catalysts are shown in Fig. 9. The objective was to decrease the concentration of the expensive hypophosphite catalyst needed, by using as co-catalysts or extenders certain inexpensive phosphates or polyphosphates. In this we were successful, since a high level of performance and laundering durability were obtained with as little as 0.8 hypophosphite. The physical properties imparted by two of the finishes are shown in Fig. 10. They compare well with properties imparted by BTCA in the presence of 3.3% hypophosphite as already noted in Fig. 8.

We are currently engaged in further catalyst development for BTCA finishes, seeking particularly to minimize the adverse effect of sodium hypophosphite on the depth of shade imparted by sulfur dyes. With a number of other classes of dyes, the hypophosphite shows little effect on shade of dye.

POLYCARBOXYLIC ACIDS AS CH_2O -FREE DP REAGENTS



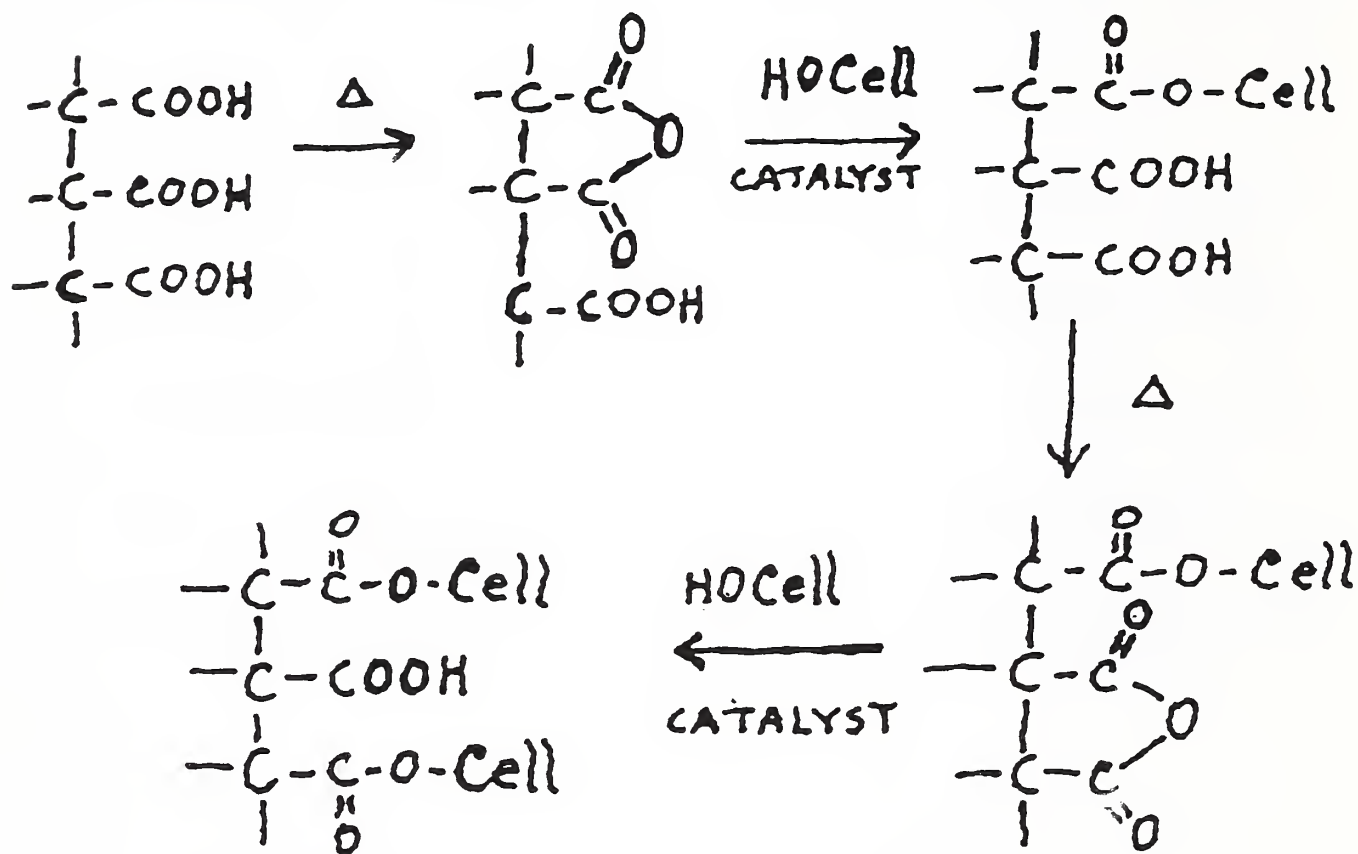
1,2,3-PROPANE-
TRICARBOXYLIC
ACID



1,2,3,4-BUTANE-
TETRACARBOXYLIC
ACID

("BTCA")

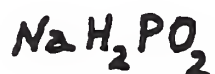
FORMATION OF ESTER CROSSLINKS



EVIDENCE FOR CYCLIC ANHYDRIDES
AS INTERMEDIATES
IN CROSSLINKING

1) WEAK BASES ARE EFFECTIVE CATALYSTS.

HYPOPHOSPHITE > PHOSPHITE > PHOSPHATE > CARBONATE



2) DICARBOXYLIC ACIDS GIVE SINGLE-ENDED
ATTACHMENT

APPLICATION OF
1,2,3,4-BUTANETETRACARBOXYLIC
ACID (BTCA)

6.3 % BTCA

SODIUM HYPOPHOSPHITE ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)

1.0 % NONIONIC POLYETHYLENE
WATER

FABRIC : 80X80 ALL-COTTON PRINTCLOTH

WET PICKUP : 120% -130% OWF

DRY : 85°C / 5 MIN.

CURE : 180°C / 90 SEC. (356°F)

RINSE : 30 MIN. (50°C)

EFFECT OF CATALYST ON DP PERFORMANCE

<u>CAT.</u> <u>CONC.</u>	<u>WT.</u> <u>GAIN</u>	CYCLES:	<u>DP RATING</u>						
			<u>(5)</u>	<u>(20)</u>	<u>(40)</u>	<u>(60)</u>	<u>(80)</u>	<u>(90)</u>	<u>(100)</u>
6.5%	12.1%		4.5	4.6	4.2	4.4	3.8	3.5	
3.3	9.9		4.4	4.6	4.4	3.8	3.5		
1.6	9.9		4.2	4.2	4.0	3.6			
0.8	10.0		3.8	4.1	3.8				
0.0	7.8		2.9						
6.5 ^a	11.3		4.5	4.6	4.4	3.9	3.8	3.6	3.6
6.5 ^{a,b}	9.9		4.6	4.4	4.4	4.0	3.7	3.7	3.8
									3.5 (120)

^a A DIFFERENT LOT OF PRINTCLOTH.

^b NO POLYETHYLENE USED.

WASH TEMP. = 122-131°F, pH = 9.8

FASTER CURING AT HIGHER TEMPERATURES^a

<u>°C</u> <u>TEMP</u>	<u>SEC.</u> <u>TIME</u>	<u>WT.</u> <u>GAIN</u>	<u>DP RATING</u> <u>(5 CYCLES)</u>	<u>DP \geq 3.5</u> <u>LAUNDERING</u> <u>DURABILITY</u> 90-100 cycles
180	90	12.1%	4.5	
180	45	11.8	4.6	86
180	30	10.8	4.0	49
195	30	11.1	4.6	84
195	20	11.0	4.6	62
195	10	10.6	4.0	21
205	20	10.7	4.6	>120
205	15	10.4	4.2	61
210	15	10.1	4.2	88
215	15	11.3	4.3	>120

^a

6.5 % CATALYST USED

USE OF LOWER WET PICKUPS^a AND LESS CATALYST

CAT. CONC.	°C TEMP	SEC. / TIME	WT. GAIN	DP (5 CYC.)	DP \geq 3.5 LAUNDERING DURABILITY
6.5 %	215	15	8.4 %	4.6	103 cycles
3.3	215	15	7.6	4.0	95
3.3	215	20	8.4 (7.6) ^b	4.4 (4.4) ^b	104 (58) ^b
3.3	205	15	8.4	4.0	39
6.5	205	20	9.5	4.6	> 118

^a 85-94 % WET PICKUPS O.W.F.

^b 1,2,3-PROPANETRICARBOXYLIC ACID (6.3%)
IN PLACE OF 6.3% BTCA

TEXTILE PROPERTIES ^a

<u>CPD.</u>	<u>°C</u> <u>TEMP</u>	<u>SEC.</u> <u>TIME</u>	<u>DP</u>	<u>(W+F)</u> <u>WRA</u>	<u>RETAINED</u>		<u>BENDING</u> <u>MOMEN</u>
					<u>%</u> <u>B.S.</u>	<u>%</u> <u>T.S.</u>	
BTCA	180	90	4.5	293	51	55	3.3 x 10 ⁶
	215	15	4.0	292	50	54	3.9
	215	20	4.4	301	53	51	3.8
PTCA	215	20	4.4	292	51	57	3.6
<u>(UNTREATED)</u>			1.0	202	(100)	(100)	5.6
^a 3.3 % NaH ₂ PO ₄ · H ₂ O			CATALYST				

MIXED CATALYSTS

0.8% $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ Na HYPOPHOSPHITE (H)

3.4% $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ Na ACID PYROPHOSPHATE (A)

4.2% $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ MONO-Na PHOSPHATE (M)

4.1% $\text{Na}_4\text{P}_2\text{O}_7$ + 1.5% H_3PO_4 (T)

<u>CAT.</u>	<u>°C</u> <u>TEMP</u>	<u>SEC.</u> <u>/TIME</u>	<u>WT.</u> <u>GAIN</u>	<u>DP</u> <u>(5 CYC.)</u>	<u>DP ≥ 3.5</u> <u>LAUNDERING</u> <u>DURABILITY</u>
H	215	15	6.9	2.8	0 CYCLES
A	215	15	8.3	3.2 ^a	3
H+A	215	15	9.4	4.2	36
	215	20	10.0 (7.2) ^b	4.1 (3.2) ^b	81 (0) ^b
	210	20	11.0	3.9	65
M	215	20	8.5	4.2 ^a	—
H+M	215	20	9.0	4.2	69
H+T	215	15	10.8	3.9	57

^a

FABRIC YELLOWED

^b

1,2,3-PROPANETRICARBOXYLIC ACID

TEXTILE PROPERTIES^a

<u>CO-CATALYST</u>	<u>DP</u>	<u>(W+F)</u> <u>WRA</u>	<u>RETAINED</u>		<u>BENDING MOMENT</u>
			<u>%</u> <u>B.S.</u>	<u>%</u> <u>T.S.</u>	
$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$	4.1	294	54	53	3.8×10^{-4}
NaH_2PO_4	4.2	294	53	53	3.7
(UNTREATED)	1.0	202	(100)	(100)	5.6

^a CURE: 215°C/20 SEC.

MULTIPURPOSE TEXTILES CONTAINING CROSSLINKED POLYETHYLENE GLYCOLS
AFFIXED BY A LOW TEMPERATURE CURE

Tyrone L. Vigo and Joseph S. Bruno

Modification of a variety of fabric and fibrous surfaces has been achieved by insolubilization of crosslinked polyethylene glycols. The resultant fabrics have improved thermal storage and release behavior, resiliency, wear life and hydrophilicity and resistance to oily soiling, pilling and static charge. Durable binding of the polyols is normally achieved by a pad-dry-cure-process utilizing polyols, DMDHEU and an acid catalyst. Processing conditions for affixing the polyols onto fabrics at low cure temperatures (85-100°C) for short curing times (0.8-5 min.) are described. Particular emphasis is given to treatment of cellulosic and cellulosic blend fabrics under these conditions. Resultant fabrics have better thermal activity and greater improvements in many other functional properties than those cured by earlier, two-step dry and cure processes at higher cure temperatures (>100°C). Dramatic increases in flex life (300-1,000%) and substantial increases (100-300%) in flat abrasion characteristics were observed for many of the nonwoven and woven fabrics containing bound polyols. Selective crosslinking of the amorphous regions of the polyols under mild conditions is proposed as the reason for beneficial changes produced in several functional fabric properties.

FABRICS/SUBSTRATES

WOVEN COTTON

CELLULOSIC/PET BLENDS

Nonwoven Paper/PET

Woven and Nonwoven Cotton/PET

NONWOVEN MELT-BLOWN POLYPROPYLENE

CHEMICALS USED

POLYETHYLENE GLYCOLS (PEG)

M_n 1,000; 1,450

40% DMDHEU

5/1 MOLAR RATIO

$MgCl_2 \cdot 6H_2O$ /citric acid

NaCl

PAD BATH SOLUTION

50% PEG
11-13% DMDHEU
3-4% CATALYST
0-5% NaCl

% WET PICKUP VARIES
WITH CONSTRUCTION
(60-380%)

PAD/DRY/CURE PROCESS
TO INSOLUBILIZE POLYOL
ON FIBER

DRY/CURE 0.8-6.0 MIN
80-100C

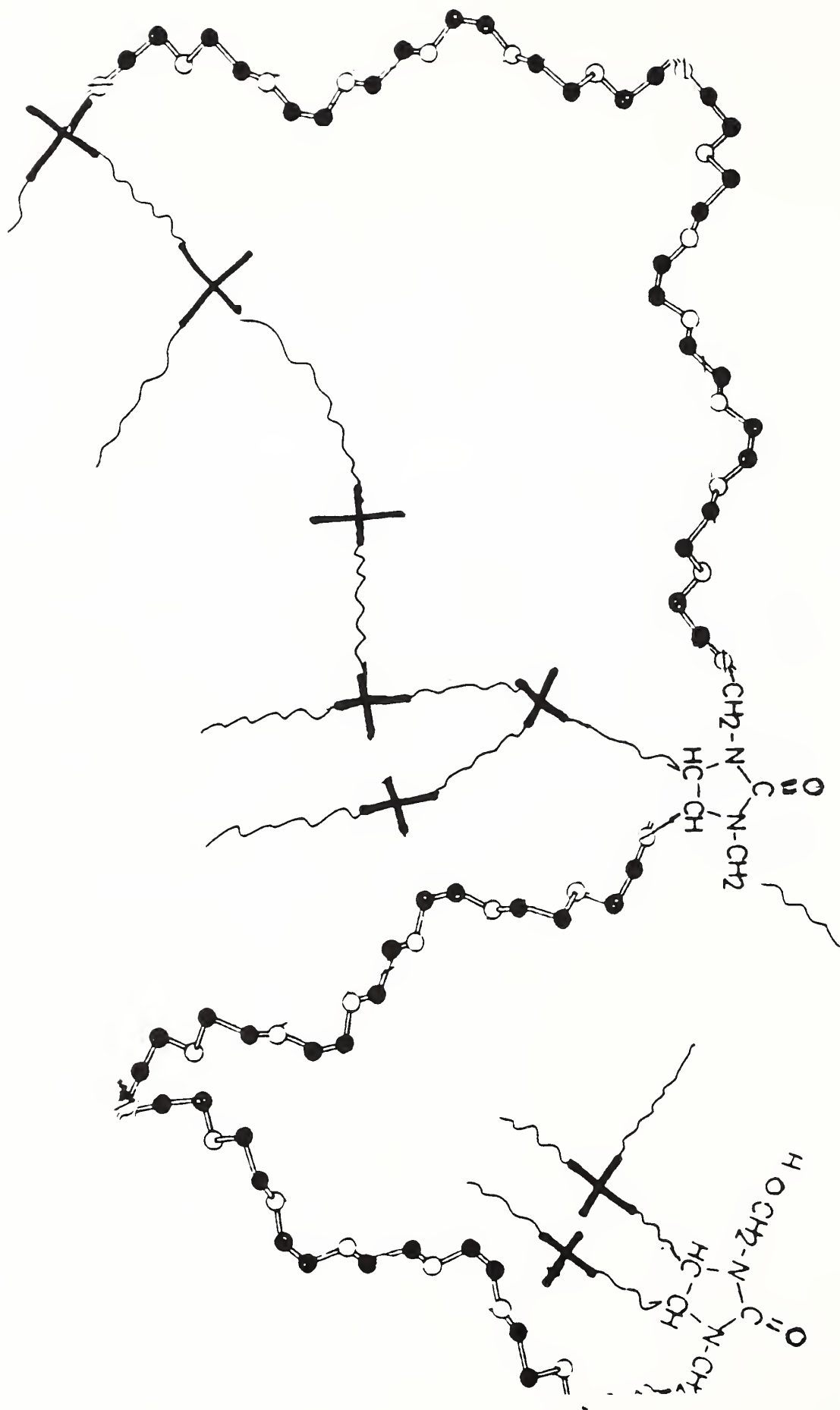
WASHED 30 MIN/60C
TUMBLE-DRIED

EXAMPLES WEIGHT GAINS WITH DIFFERENT SUBSTRATES
& CURING CONDITIONS (PEG-1000/RESIN)

SUBSTRATE	CURE TIME MIN	CURE TEMP. (C)	% WT. GAIN
100% WOVEN COTTON PC	5	80	30
	3	90	40
	1.5	100	29
	5	100	52
55/45 PAPER/PET NONWOVEN	1.5	90	46
	3	90	87
	0.8	100	2
	1.5	100	75
100% MB POLYPROPYLENE NONWOVEN	0.8	100	28
	1.5	100	182

EXAMPLES WEIGHT GAINS WITH DIFFERENT SUBSTRATES
& CURING CONDITIONS (PEG-1450/RESIN)

SUBSTRATE	CURE TIME MIN	CURE TEMP. (C)	% WT. GAIN
75/25 C/PET NONWOVEN	0.8	100	0
	3	100	96
	5	100	101
55/45 PAPER/PET NONWOVEN	0.8	100	2
	1.5	100	62
	5	100	87
100% MB POLYPROPYLENE NONWOVEN	0.8	100	65
	1.5	100	154
	5.0	100	166

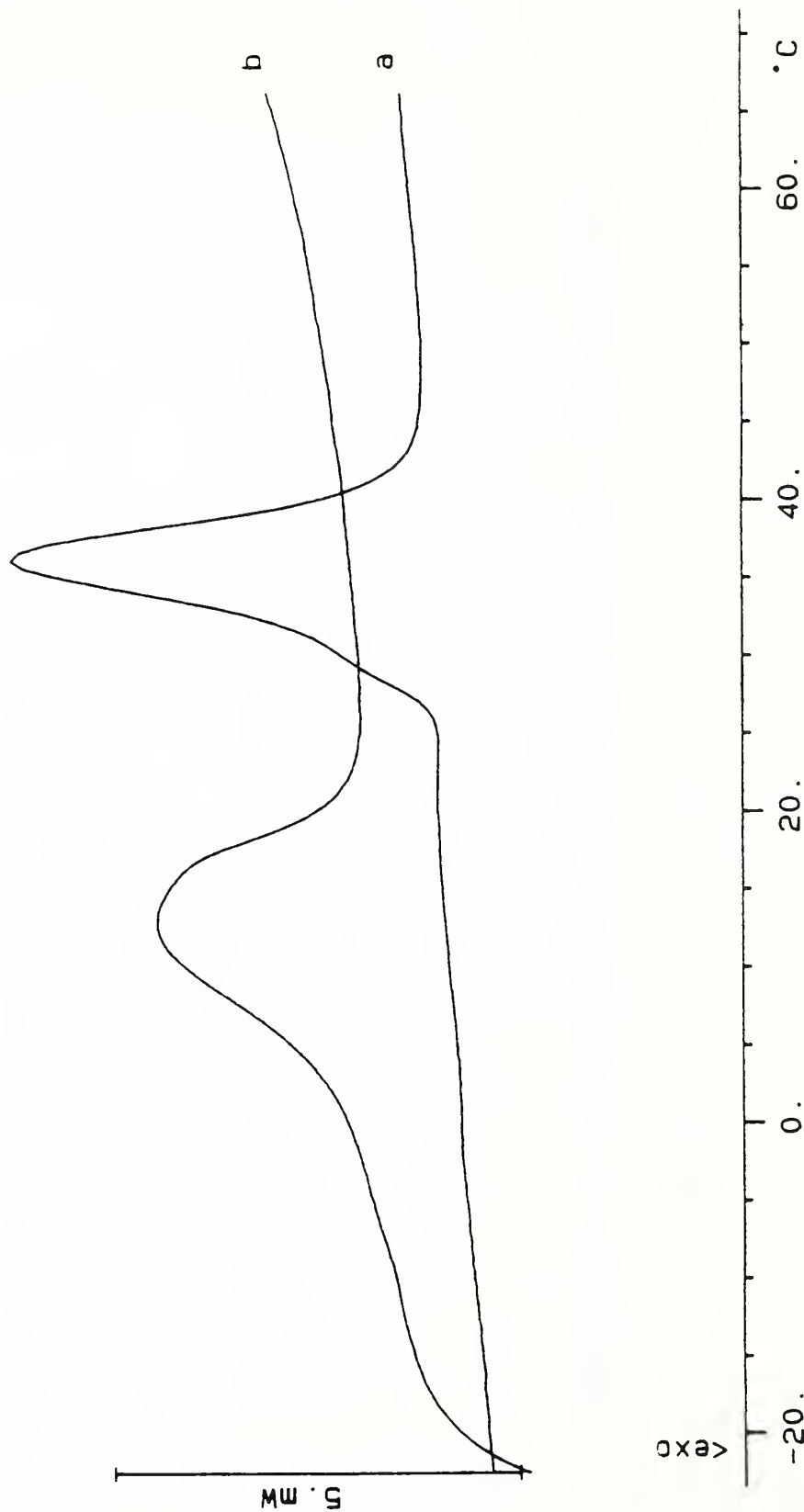


TEXTILE PROPERTIES IMPARTED OR IMPROVED
BY PROCESS

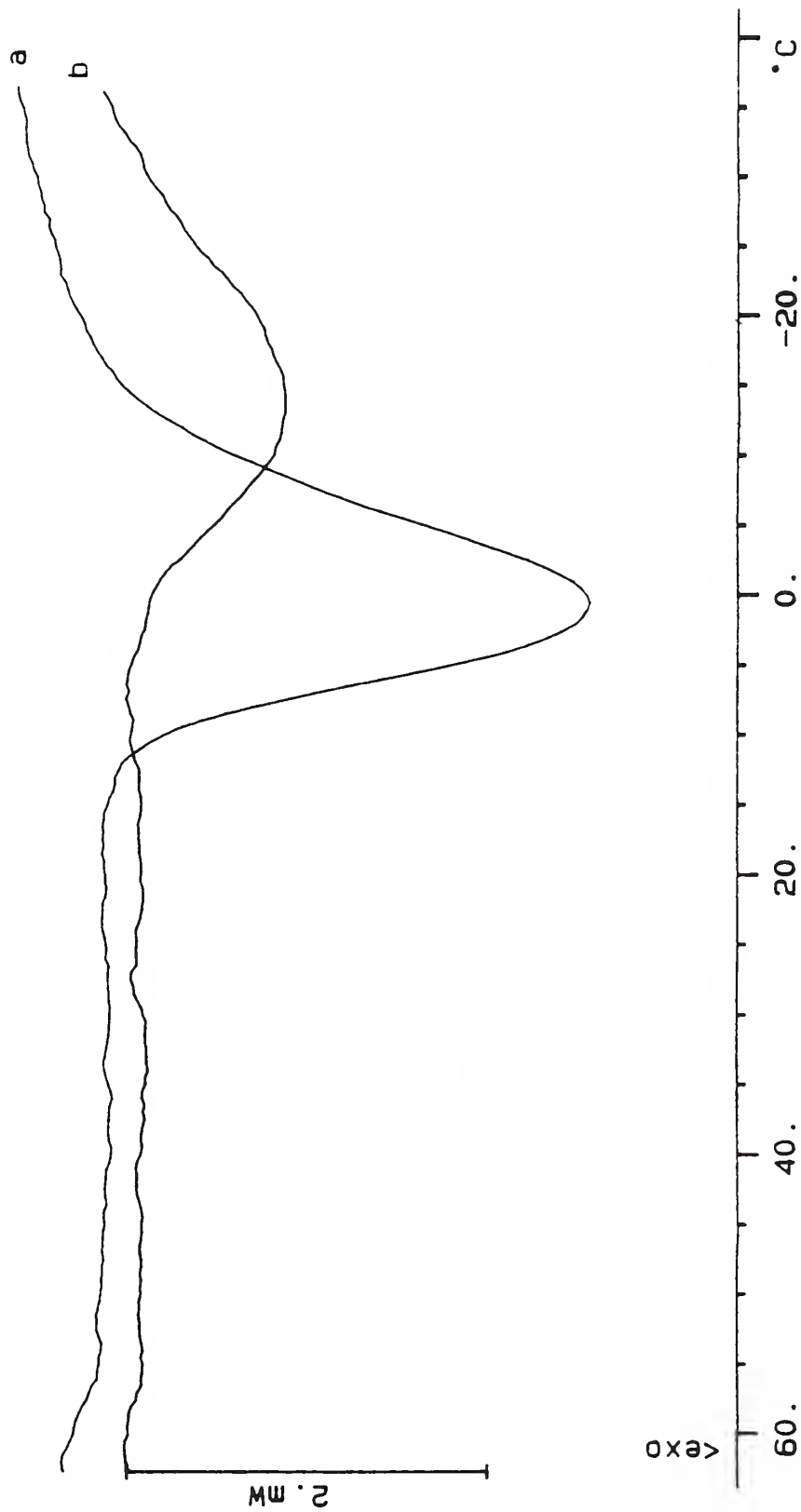
THERMAL STORAGE AND RELEASE
EXTENSIBILITY/WEAR
WATER ABSORBENCY/CAPACITY
RESILIENCY/DRY WRINKLE RECOVERY
PILLING RESISTANCE
ANTISTATIC
SOIL RELEASE

DURABILITY OF FINISH TO REPEATED LAUNDERING

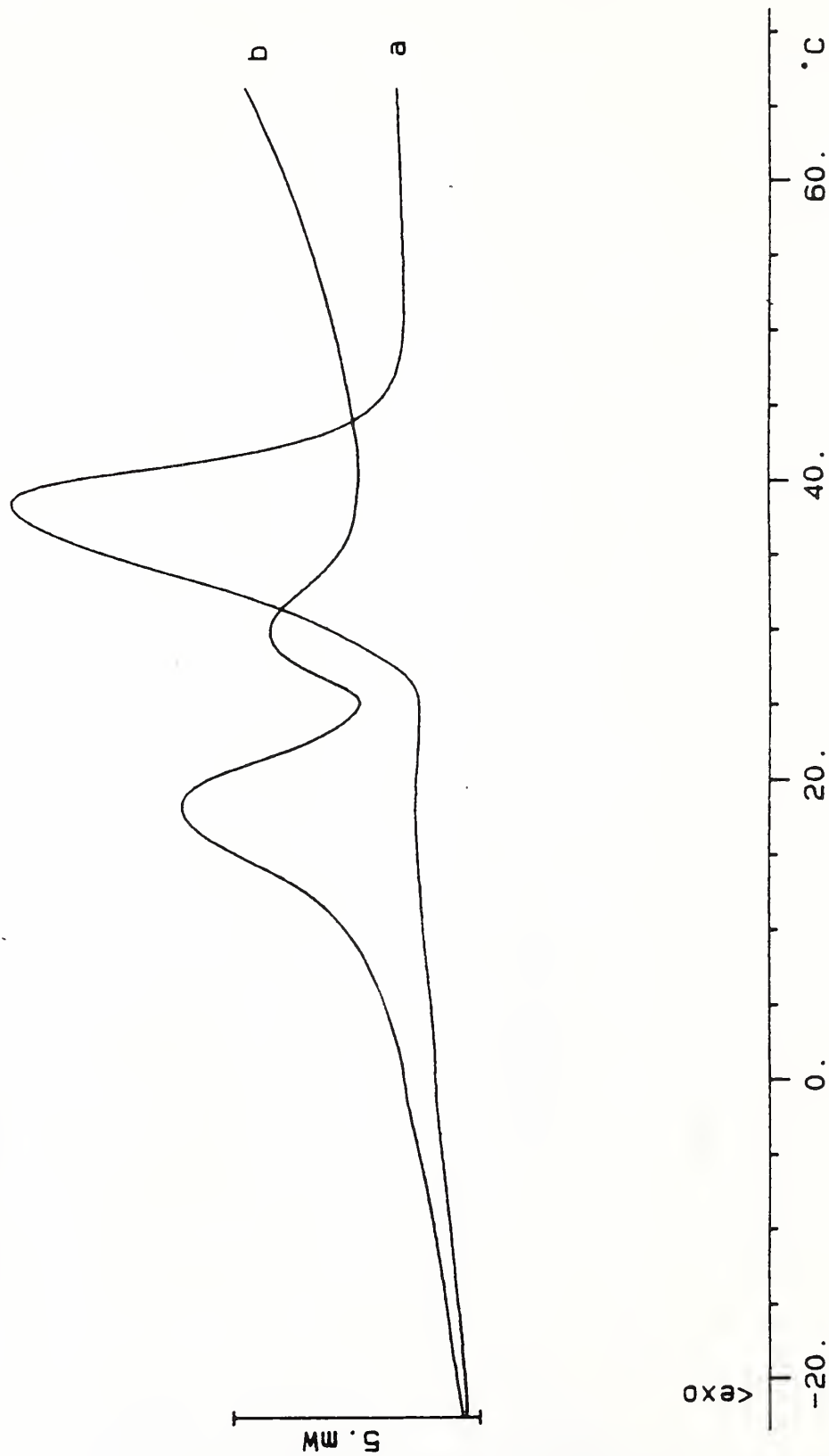
HEATING SCANS OF NONWOVEN PAPER/PET
TREATED WITH PEG-1000/DMDHEU CURED
(a) 1.5 MIN/90C/(b) 3 MIN/90C



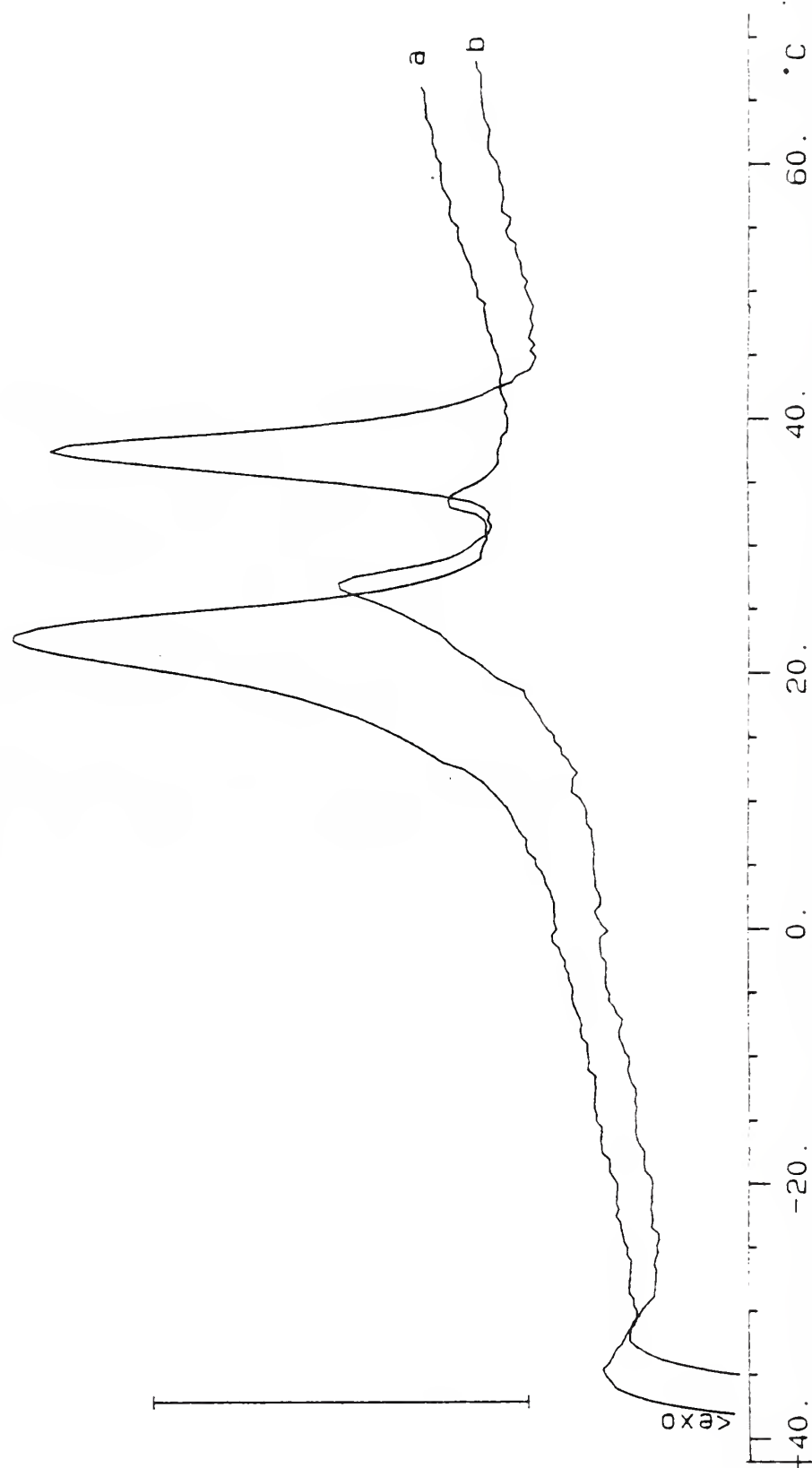
DSC cooling scans (10C/min) of melt-blown polypropylene treated
with PEG-1000/DMDHEU and dried/cured (a) 1.5 min/90C and (b) 5 min/100C.



DSC heating scans (10C/min) of cotton/polyester fabric treated with
PEG-1450/DMDHEU and dried/cured (a) 3 min/90C and (b) 5 min/100C.



**HEATING SCANS OF WOVEN 50/50 COTTON/PET
TREATED WITH PEG-1450/DMDHEU CURED
(a) 3 MIN/90C/(b) 3 MIN/85C**



**MECHANICAL PROPERTIES IMPROVED
WITH MINIMUM CURING CONDITIONS**

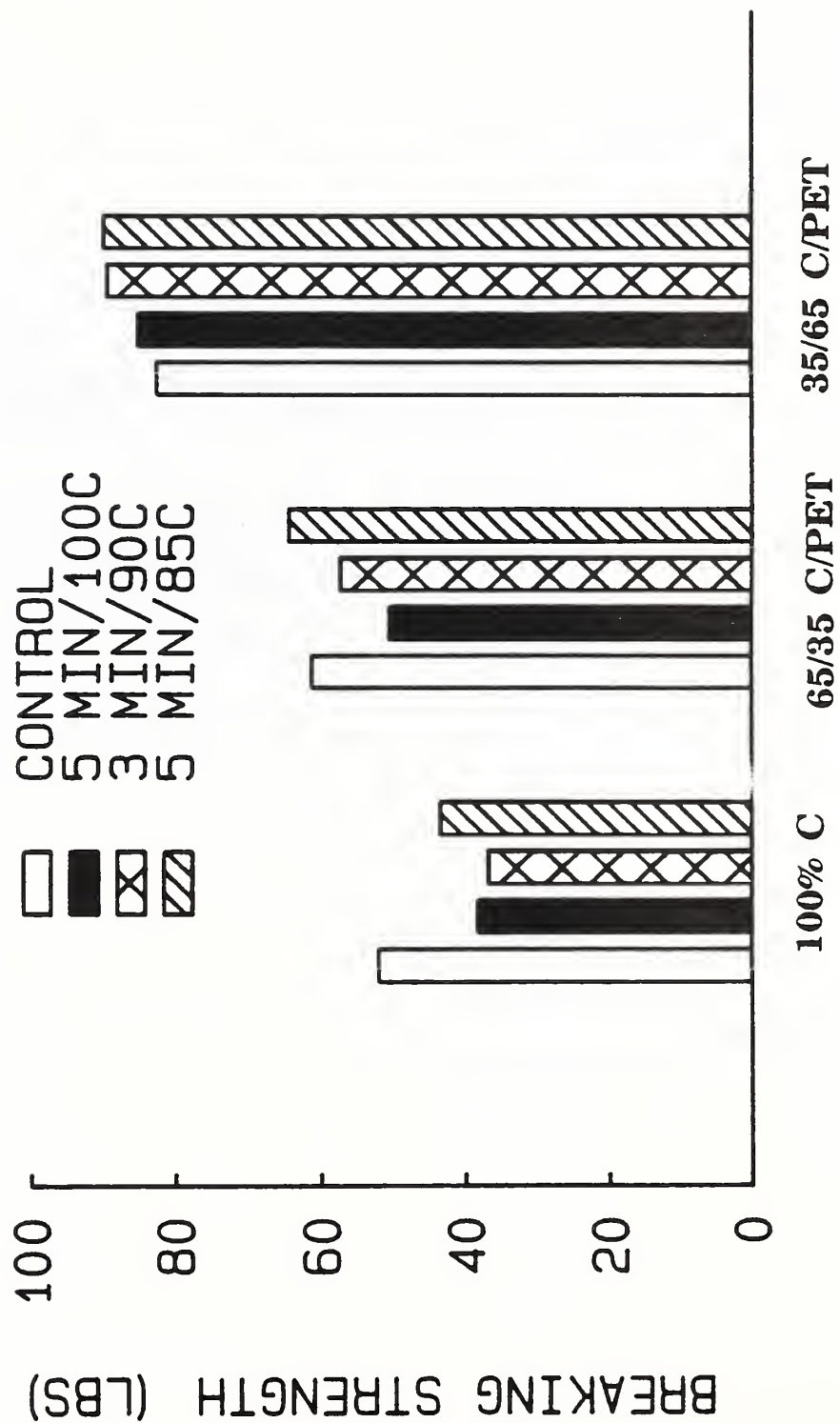
**NONWOVENS HAD INCREASES 50-100%
IN BURSTING STRENGTH
RELATIVE TO CONTROLS**

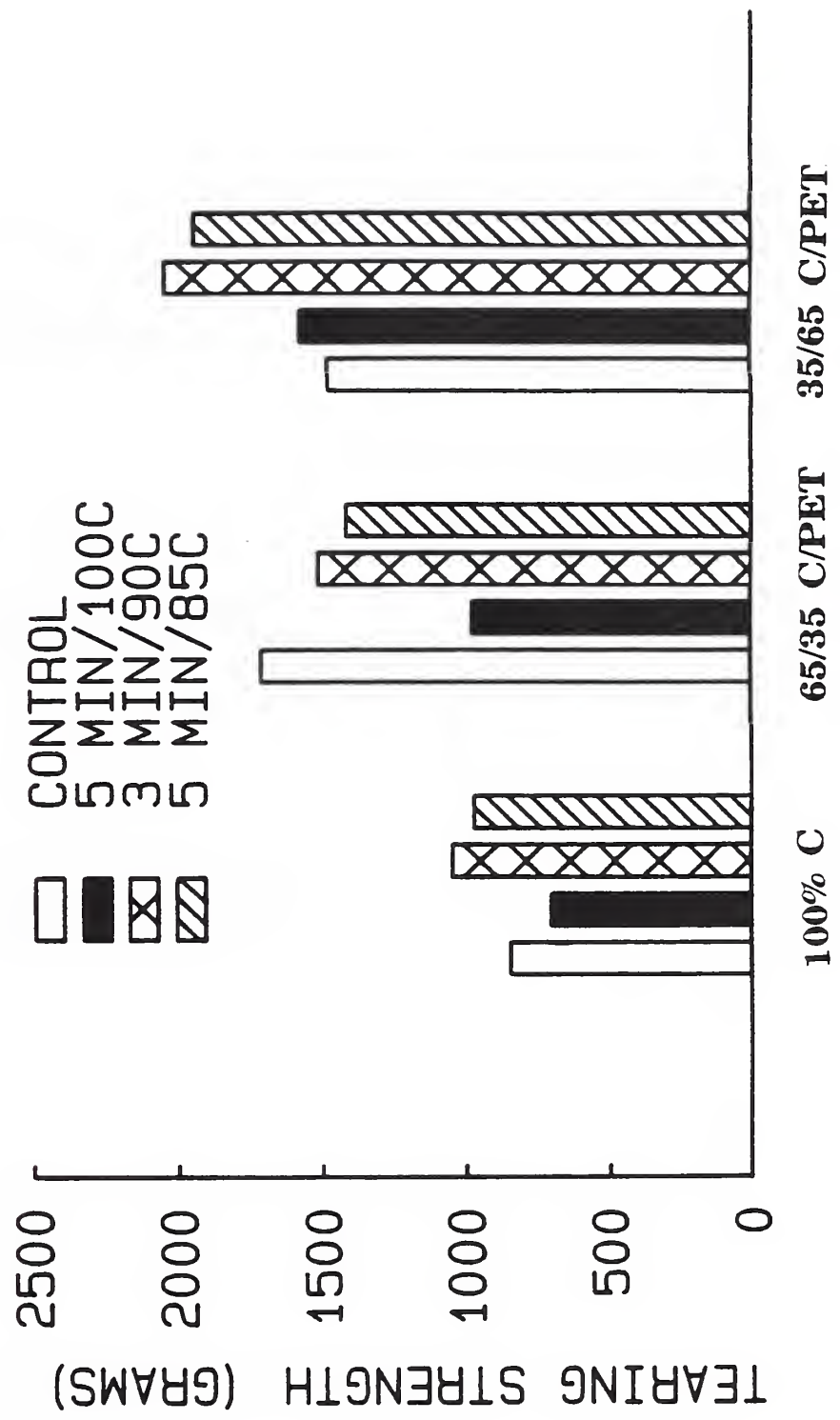
**WOVENS RETAINED 70-100%
BREAKING STRENGTH**

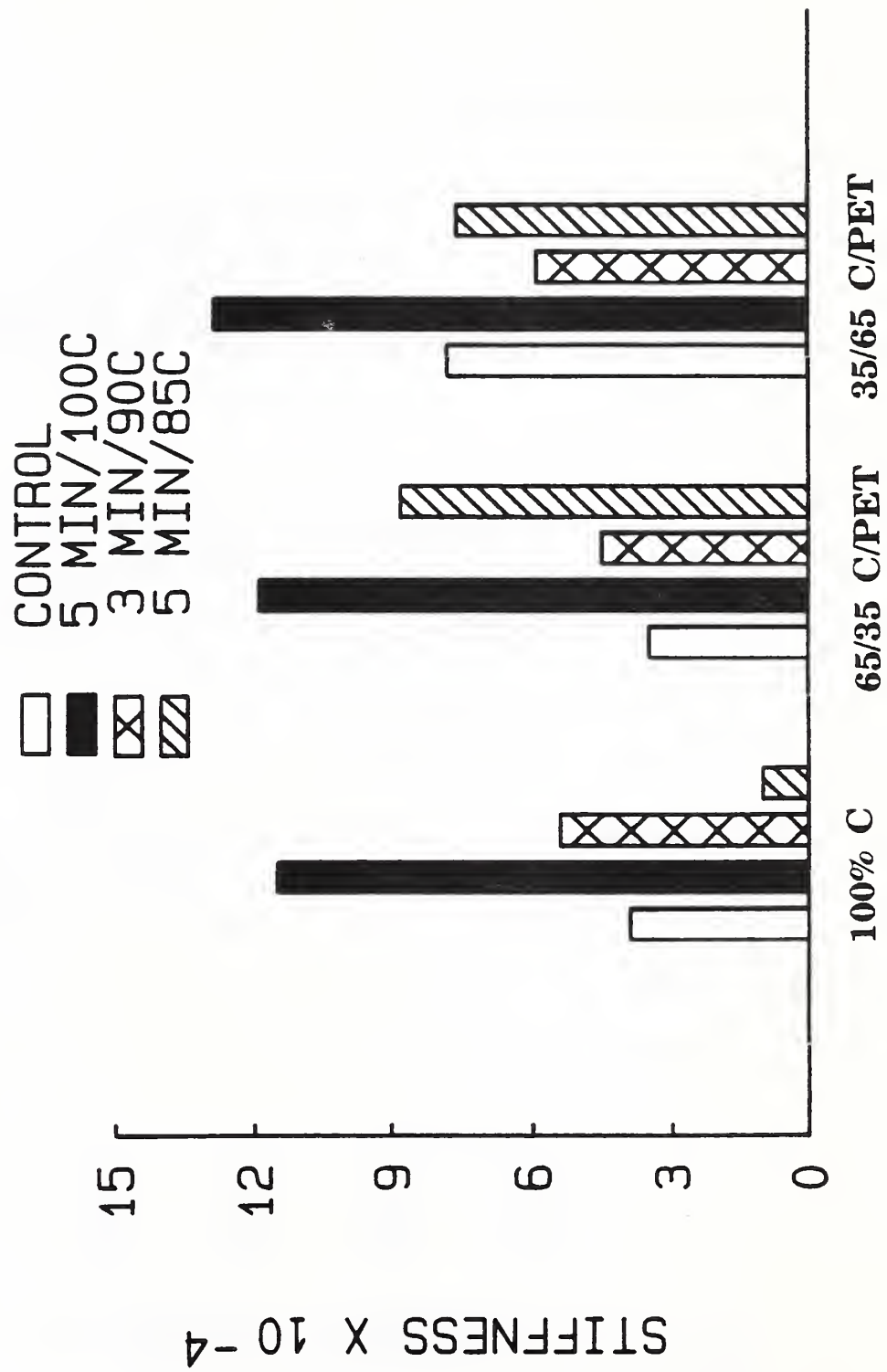
**STIFFNESS USUALLY GREATER
FOR TREATED WOVEN FABRICS
BUT SOME WOVENS HAD GOOD HAND**

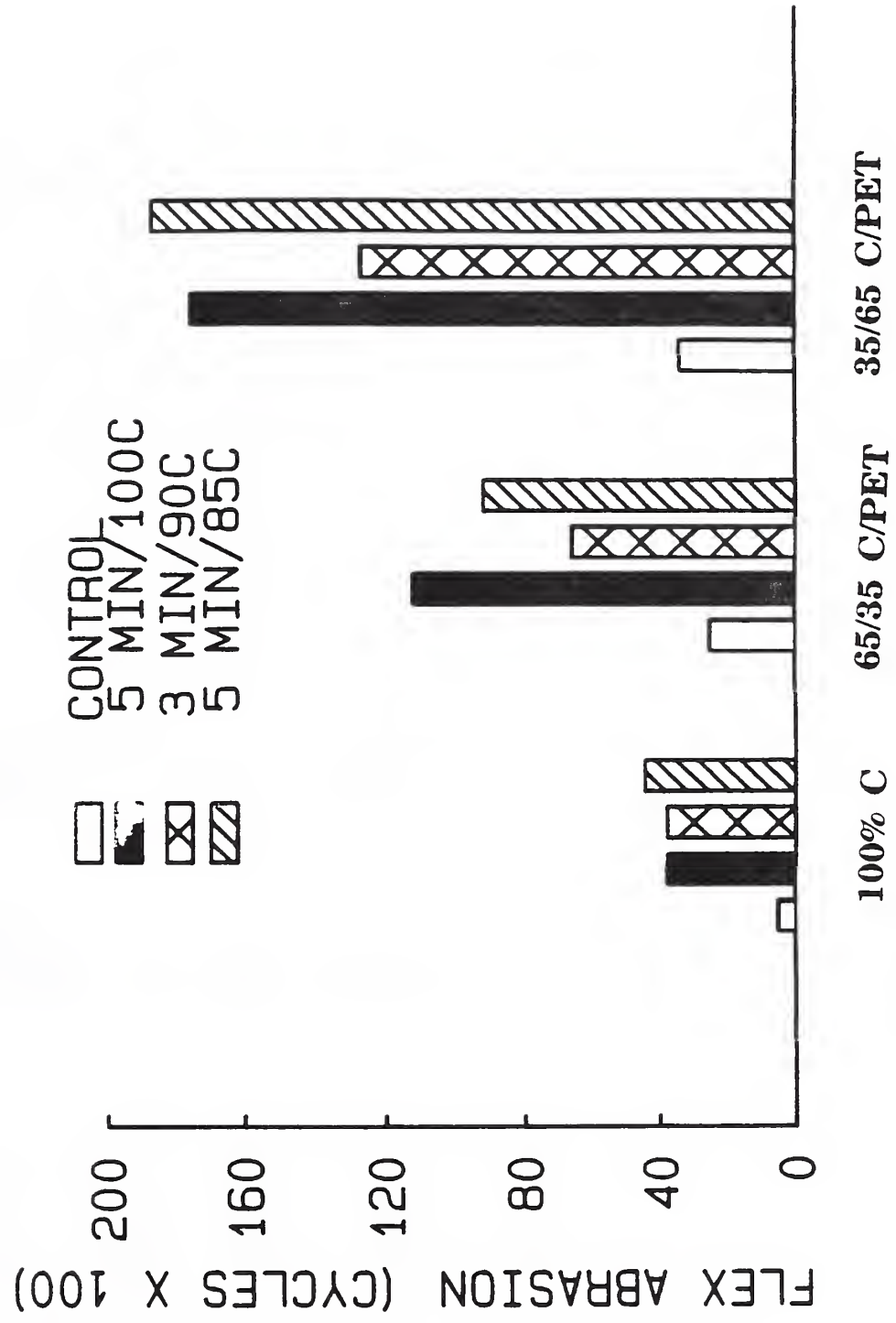
**ABRASION (FLEX AND FLAT)
TREATED WOVEN FABRICS
IMPROVED 100-800%
RELATIVE TO CONTROLS**

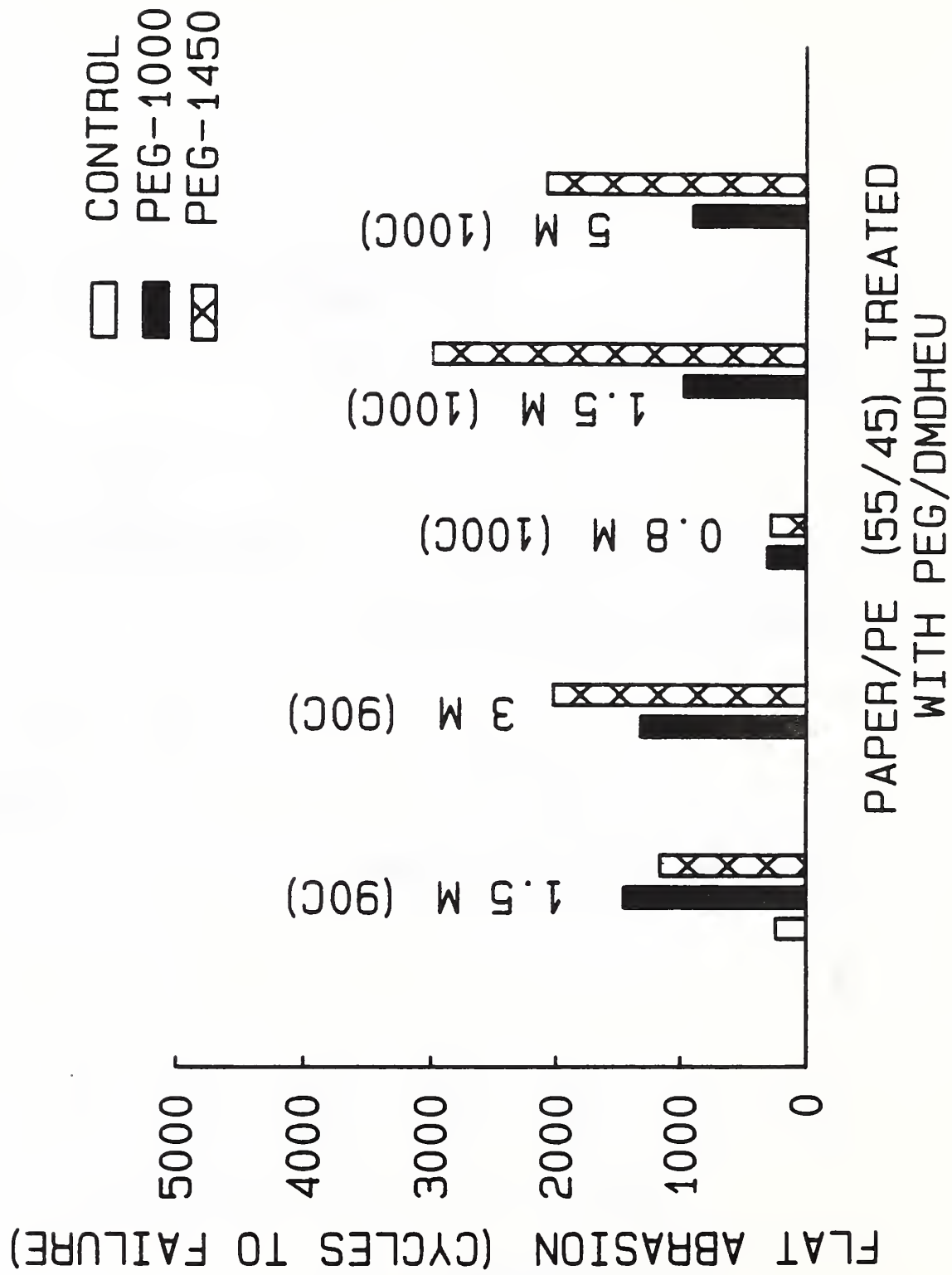
**ABRASION TREATED NONWOVENS
IMPROVED PRIMARILY IN
PAPER/PET (FLAT AND FLEX)
AND IN COTTON/PET (FLAT ONLY)**

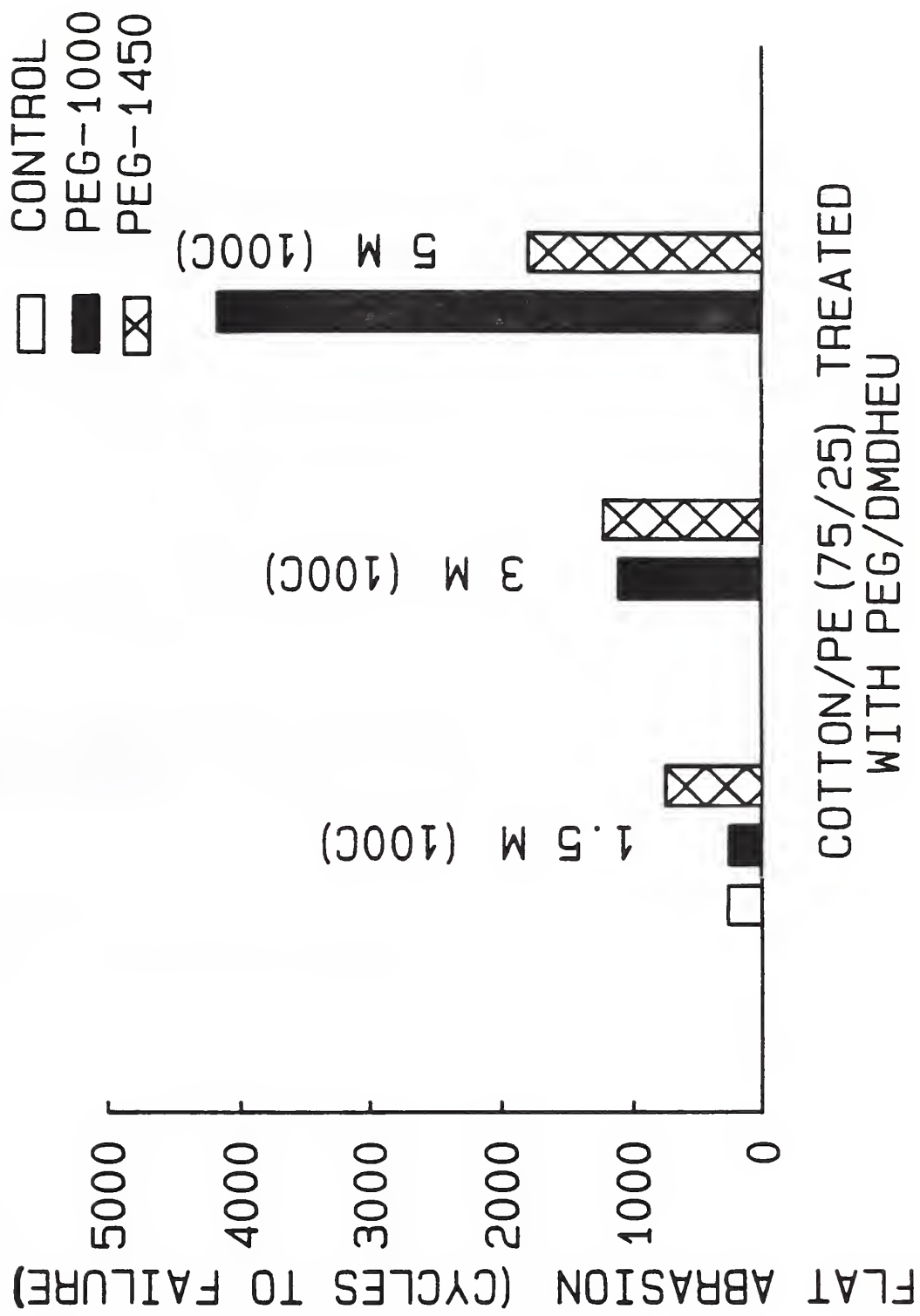


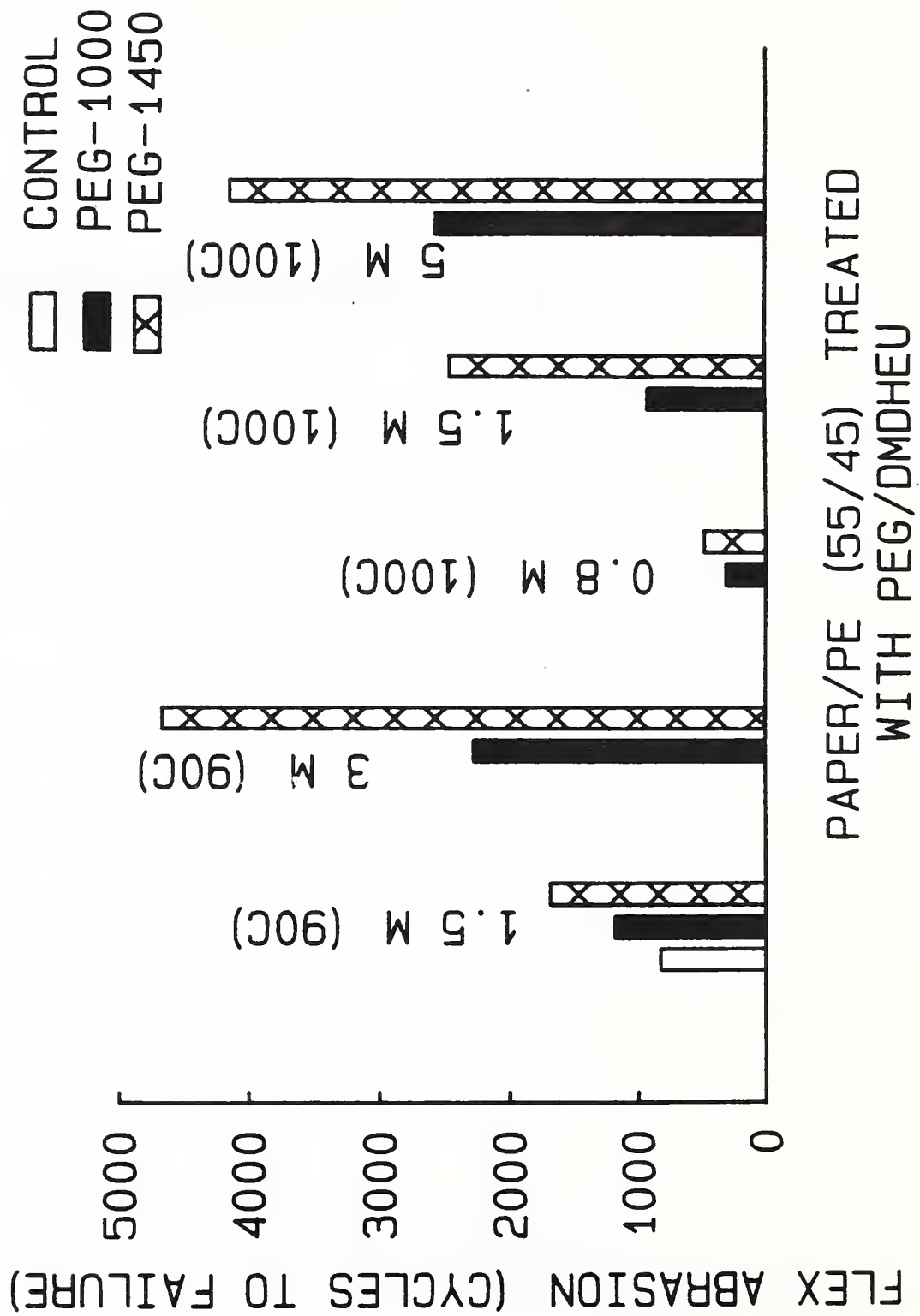












SUMMARY AND CONCLUSIONS

**CROSSLINKED POLYOLS BOUND TO
FABRICS/SUBSTRATES AT
LOW CURE TEMP. GIVES**

**HIGHER T_m and T_c
HEAT CONTENTS**

**DRAMATIC IMPROVEMENTS IN
FLEX ABRASION**

**RETAINED/IMPROVED STRENGTH
HAND, TOUGHNESS**

**SELECTIVE CROSSLINKING OF
POLYOLS IN AMORPHOUS
REGIONS OF THESE SEMI-CRYSTALLINE
POLYMERS CONTRIBUTES TO
THESE ENHANCED PROPERTIES AND
ATTRIBUTES**

FTIR CHARACTERIZATION OF FABRICS CONTAINING CROSSLINKED POLYETHYLENE GLYCOLS

Nancy M. Morris

The topic of this investigation is an infrared study of polyethylene glycol treated fabrics at various temperatures. To put our investigation of new polymers, catalysts, curing conditions and other factors on a more systematic and less empirical basis, we have begun the study of structural changes of the polymer system with changes in temperature. We hope that determination of those structural changes that are associated with the most desirable properties or combination of properties will enable us to learn how these polymers behave on heating and we will be able to use this information to improve our selection of polymer and/or treatment conditions.

The fabrics used in this study are shown in Fig. 1. They were treated according to the conditions shown in Fig. 2 and wet pick-up and weight gains are shown in Fig. 3. The dried fabrics were ground in a Wiley mill to pass a 20-mesh screen and potassium bromide disks were prepared from the treated fabric. Infrared spectra were obtained over a temperature range of 25°C to 220°C. We used a temperature cell manufactured by RIIC (Research and Industrial Instruments Corporation) to obtain the spectra at various temperatures (Figs. 4 and 5). This cell can be varied from sub-ambient temperatures (liquid nitrogen) up to 250°C.

Differences in the spectra with temperature were observed (Fig. 6). To aid in the interpretation of the spectral differences, all spectra were imported into the SpectraCalc software program by Galatic Industries and various difference spectra were compared.

Fig. 7 shows the spectrum of both treated and untreated woven 100% cotton print cloth at ambient temperature (25 degrees) with the 50 degree spectrum subtracted. These spectra show that both fabrics exhibit differences on heating 25 degrees. In the OH stretching region, the untreated fabric shows a strong intermolecularly hydrogen-bonded peak. There is an increase in the peaks at about 3400 wavenumbers in the treated fabric. This could indicate that the reaction between the cellulosic hydroxyl groups and the crosslinked polyethylene glycol changes the nature and/or degree of hydrogen bonding and produces a shift toward the free OH stretching region. Similar changes were observed for the other fabrics in this study.

To further study the effect of heating on the infrared spectra of these fabrics, the spectrum of the treated fabric at elevated temperatures was subtracted from that of the treated fabric at 25°C. Fig. 8 is of treated 100% cotton print cloth at 25 °C with the 75, 150, and 200 °C spectrum subtracted. Fig. 9

shows the corresponding spectra of a 65/35 cotton polyester knit and Fig. 10 those of non-woven rayon. In each case the changes are gradual and continuous over the entire temperature range studied. This indicates that a major phase change such as melting of the polymer did not occur for these treated fabrics. It is possible that the polymer undergoes continuous expansion and uncoiling on heating. This would be consistent with the infrared data obtained for these samples. The uncoiling of the polymer may continue throughout the temperature range studied. Although a thermal transition could occur at a specific temperature, the spectral data would not necessarily show a discontinuity at that temperature unless it is accompanied by a major change in the structure.

To study the effect of heating on the polymer system itself, a film of the padding solution was cast on an Irtran plate, dried under an infrared lamp, and subjected to the same heating program as the fabrics (Fig. 11). The lack of abrupt change in the spectrum on heating indicates that for the cross-linked polymer no major structural changes accompanied the thermal transition.

A film of polyethylene glycol alone was prepared the same way as for the padding solution (Figs. 12 and 13). There was a general loss of absorbance, overall peaks becoming smaller as well as less resolved. This is consistent with results reported in the literature for other polymers. Bands in the 900 to 1100 cm^{-1} region have been reported to be very sensitive to thermal energy. These bands can result from intermolecular coupling producing the crystal lattice or from intramolecular coupling of the groups in a regular helix or coiled chain. In either case an increase in temperature disrupts the coupling. A form of structural relaxation occurs and the integrated absorbance of the bands is reduced.

Difference spectra of the PEG film with the heated spectrum subtracted from the room temperature spectrum are shown in Fig. 14. In this case there are some peaks in the CH stretching region and in the CO and CH_2 rocking regions (the 900 to 1100 wavenumber region) that increase on heating (i.e. the peaks are stronger in the spectrum of the heated film than in that of the ambient temperature film) up to a point and then reverse so that by 200 degrees these peaks are stronger in the ambient temperature spectrum. Spectra of films of catalyst alone and DMDHEU alone, prepared the same way, are shown in Figs. 15 and 16. It was determined that the decrease in absorbance on heating was not due merely to loss of polymer from the plate on heating under vacuum (Fig. 17).

The spectra are being evaluated to determine the assignments of the peaks that are changing. The spectrum of treated cotton at 200 C was subtracted from that of the treated cotton at 25 °C. In the 4000-2000 cm^{-1} region (Fig. 18) most of the peaks that are changing are in the cotton itself. Since these are difference

spectra, the larger the peak the greater the amount of change between the ambient and heated spectrum. In the 2000-450 cm^{-1} region (Fig. 19), peaks underlined are from the cotton, those circled are from the padding solution, and those double-underlined are present in the spectra of both cotton and the polymer solution. The peak at 1657 is due to adsorbed water in cellulose. From the area of this peak in the difference spectrum, it would appear that all of this water is removed by heating.

The peak assignments for polyethylene glycol are shown in Fig. 20. The literature values are for Carbowax 6000. The PEG used in this study was PEG 1000, so there was about a 6-fold difference in molecular weight. Even so the values in this study are very similar to those reported in the literature. The absorbance of most of the peaks is reduced on heating. Those assigned to the skeletal modes appeared to be reduced to a greater extent than most of the others.

In conclusion, the evidence so far points to definite changes in the absorption spectra of the polyethylene glycol treated fabrics on heating. There is a gradual and continuous change in the same direction in the spectra on heating that would indicate that the polymer structure undergoes a gradual relaxing and uncoiling which continues past the transition temperature. The fabrics and the polymer show a loss of water and production of carbon dioxide on heating.

FABRICS USED IN THIS STUDY

100% cotton print cloth

Non-woven rayon

Nylon-reinforced paper towel

50/50 cotton/polyester, woven

65/35 cotton/polyester knit

55/45 paper/polyester, non-woven

**50/50 cotton/polyester, non-woven,
thermally bonded**

FIGURE 1

PADDING CONDITIONS

The fabrics were padded, two dips, two nips, at 40 psi in the following solution:

500 g PEG 1000

275 g Hylite LF (40 % DMDHEU)

66 g mixed catalyst (50 % solution of 5:1
molar ratio of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$:Citric acid

169 g deionized water

Total 1000 g

The treated fabrics were dried and cured in one step at 100 °C.

The fabrics were washed in hot, running tap water for 30 minutes and air dried.

WET PICK-UP AND WEIGHT GAIN OF FABRICS

FABRIC	WET PICK-UP	WEIGHT GAIN
100% cotton print cloth	86.4 %	38.3 %
Non-woven rayon	88.8	32.0
Nylon-reinforced paper towel	124.8	27.1
50/50 cotton/polyester, woven	79.7	40.1
65/35 cotton/polyester knit	113.3	60.1
55/45 paper/polyester, non-woven	137.2	58.1
50/50 cotton/polyester, non-woven, thermally bonded	150.0	77.3

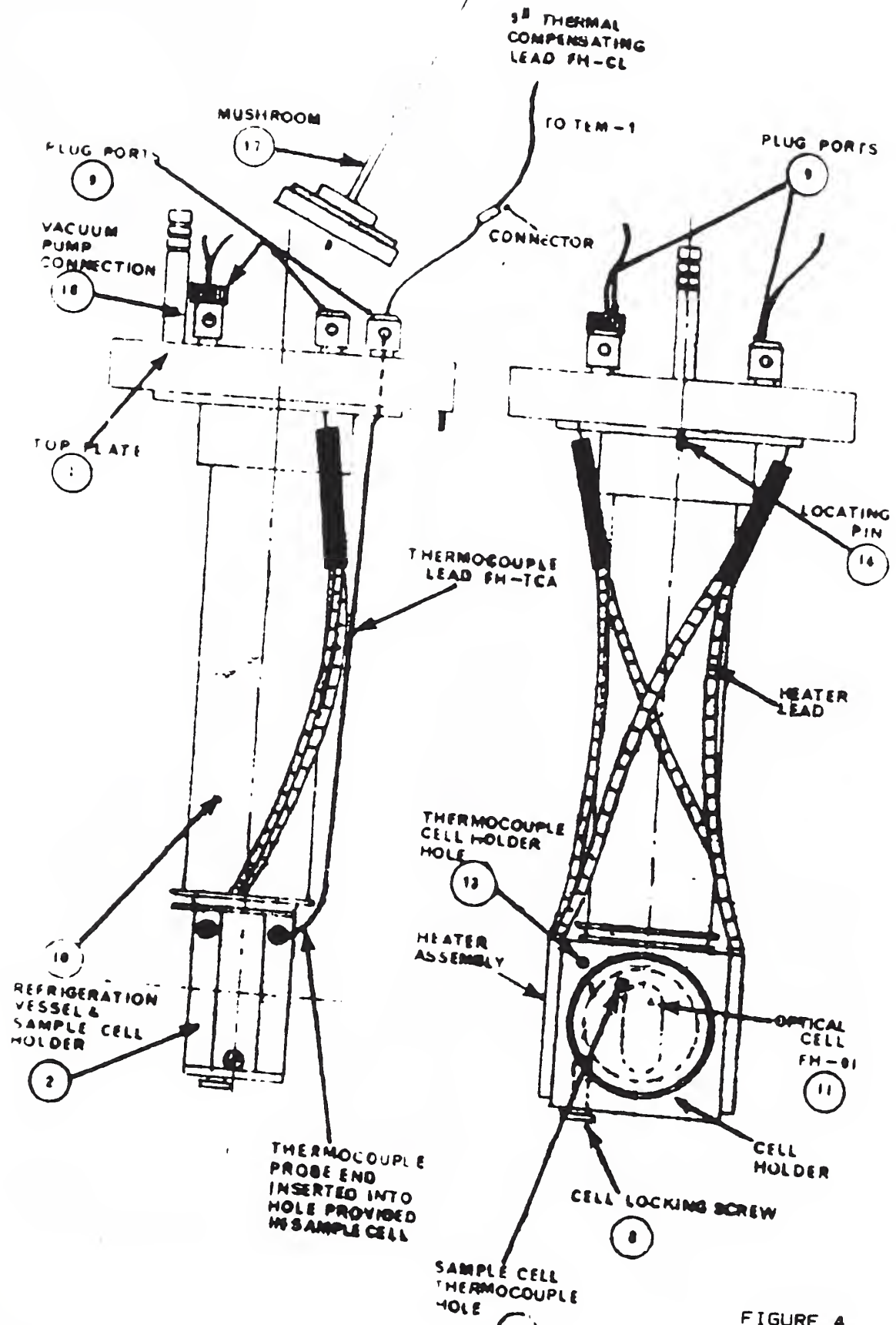


FIGURE 4

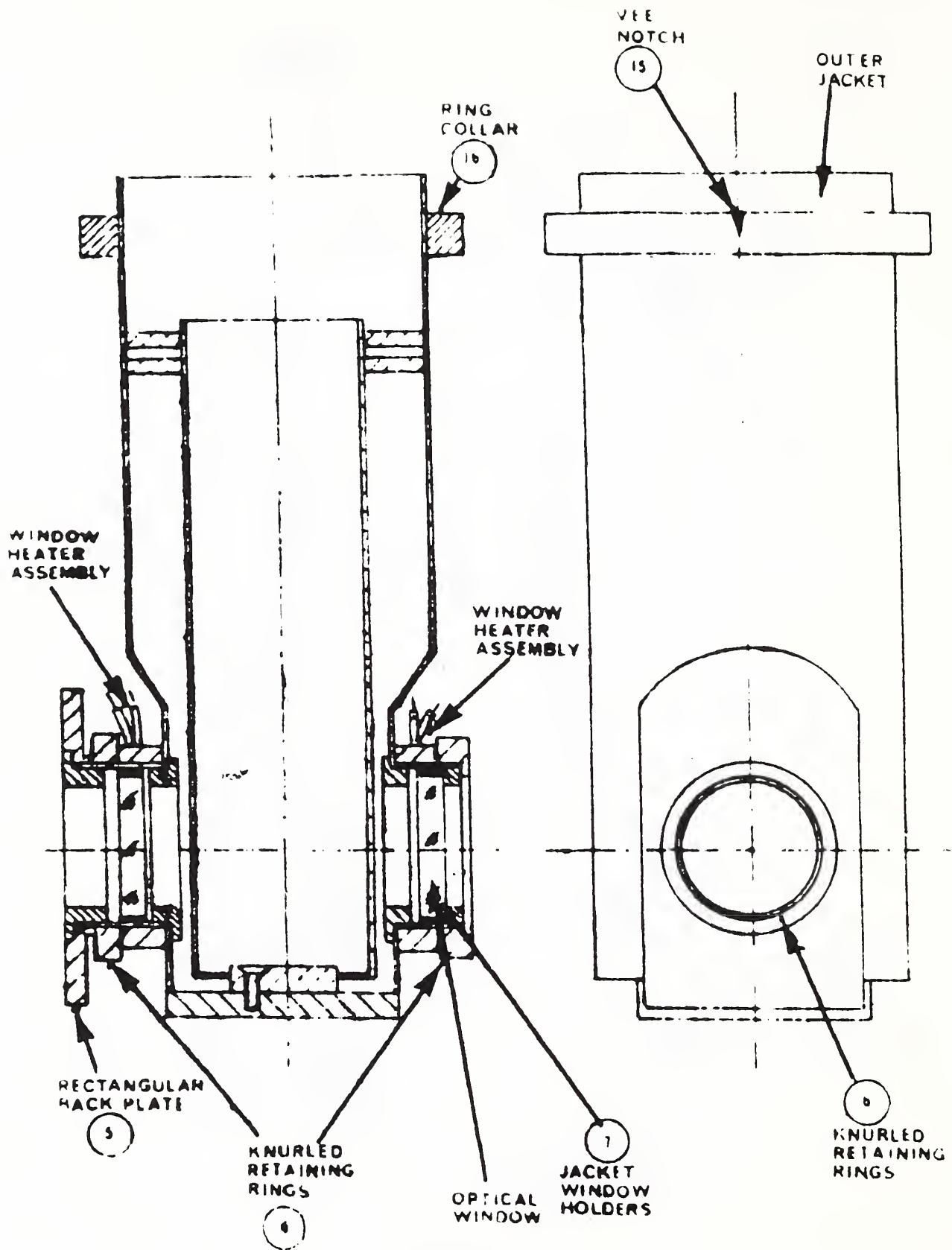


FIGURE 5

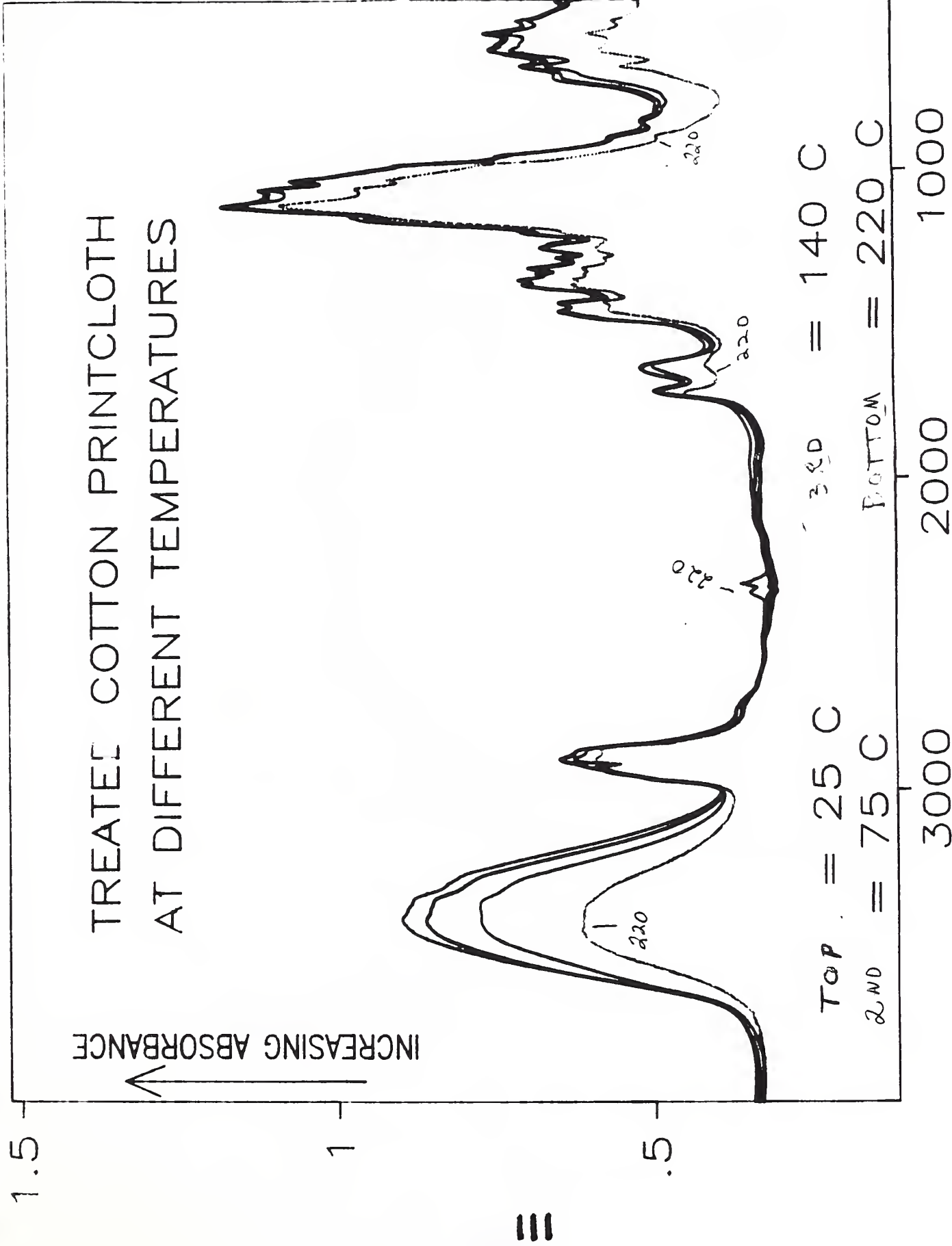


FIGURE 6

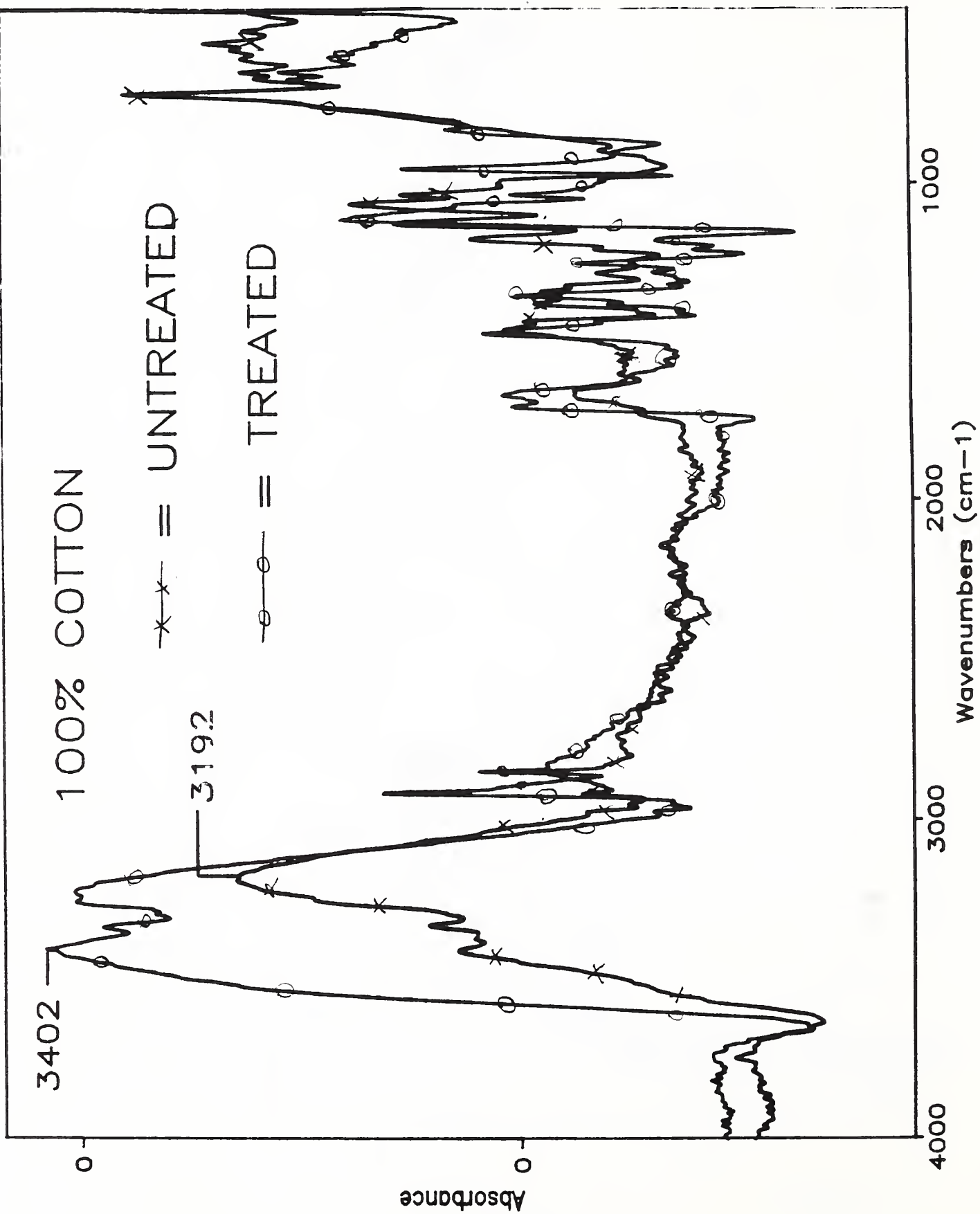


FIGURE 7

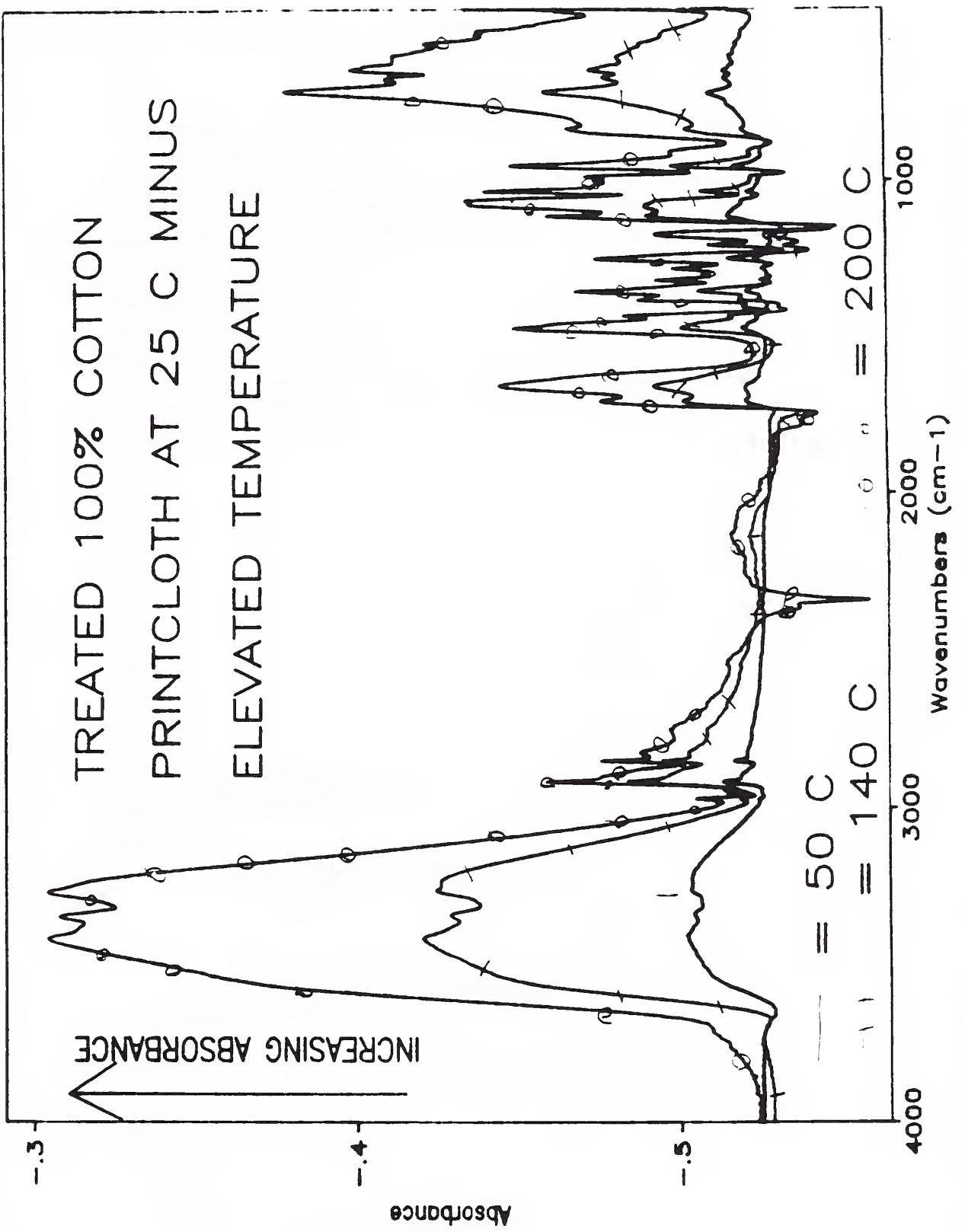


FIGURE 8

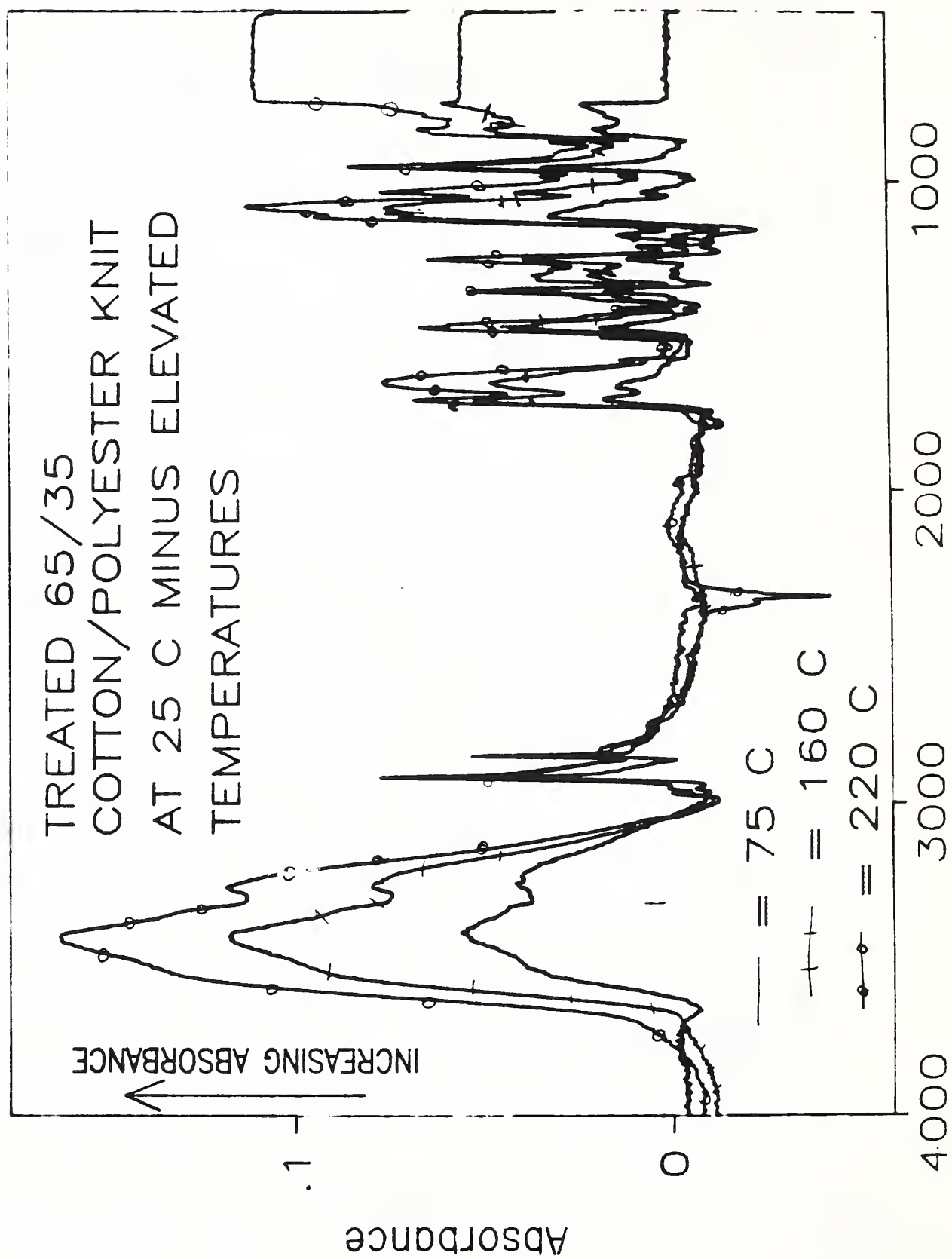


FIGURE 9

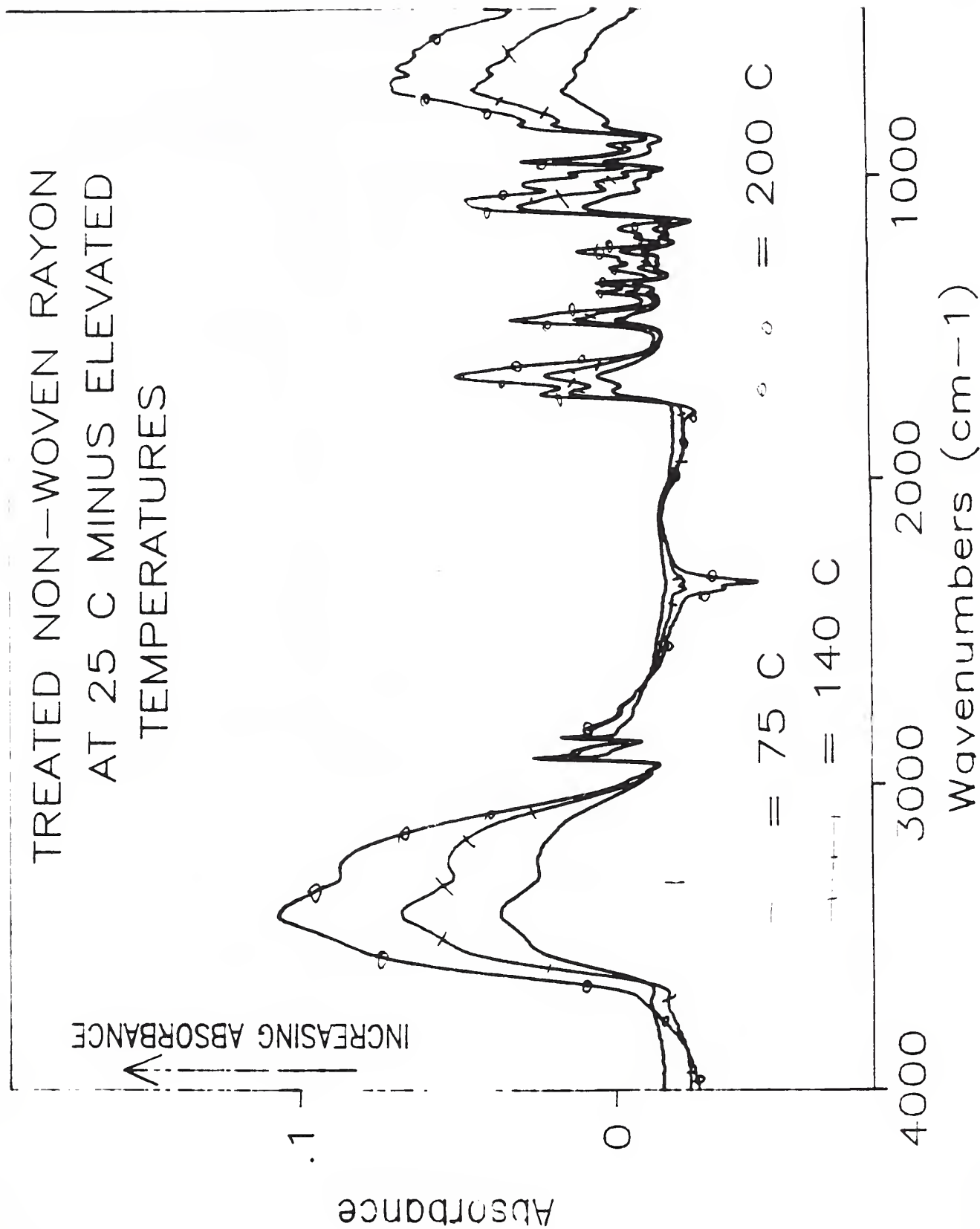


FIGURE 10

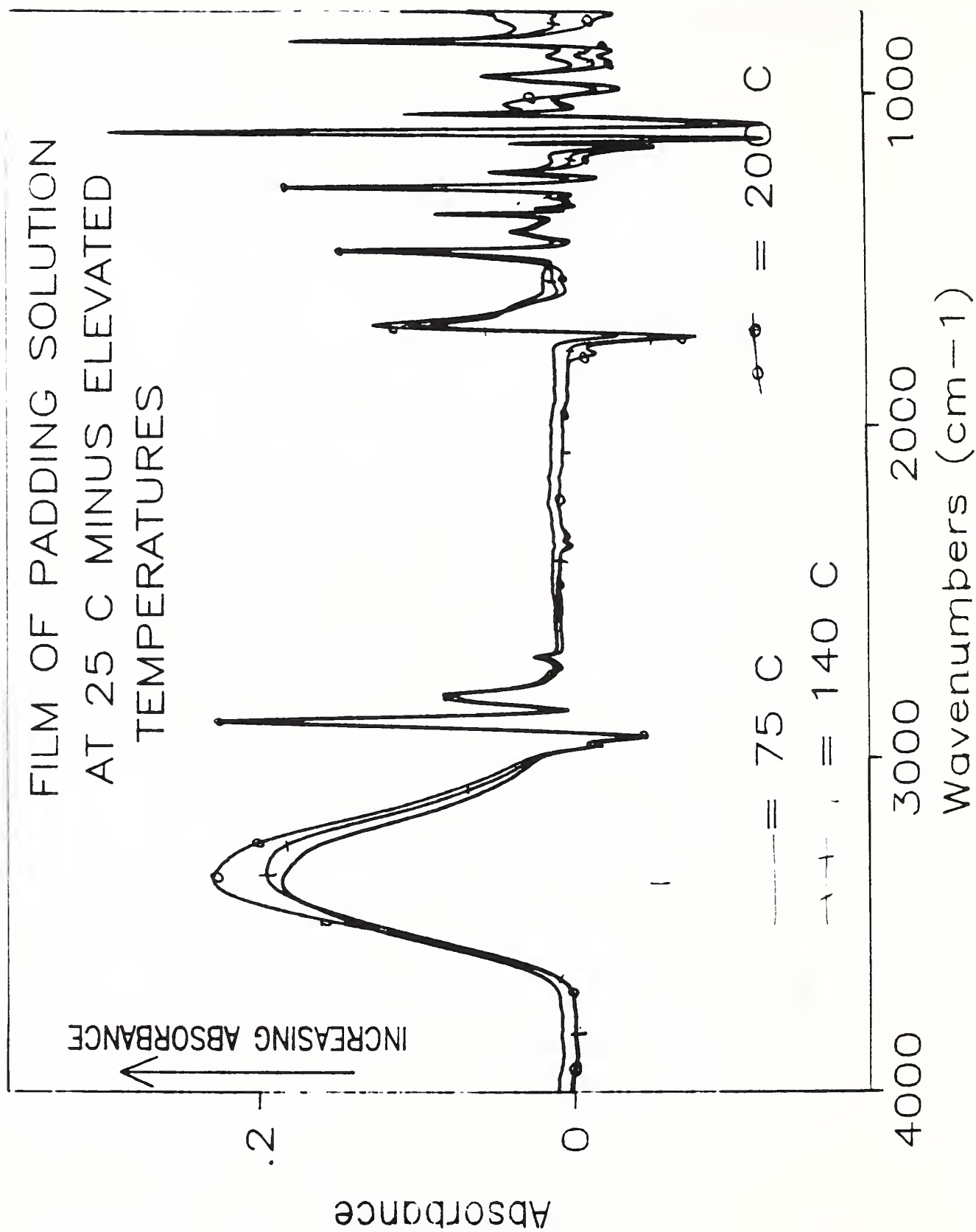


FIGURE 11

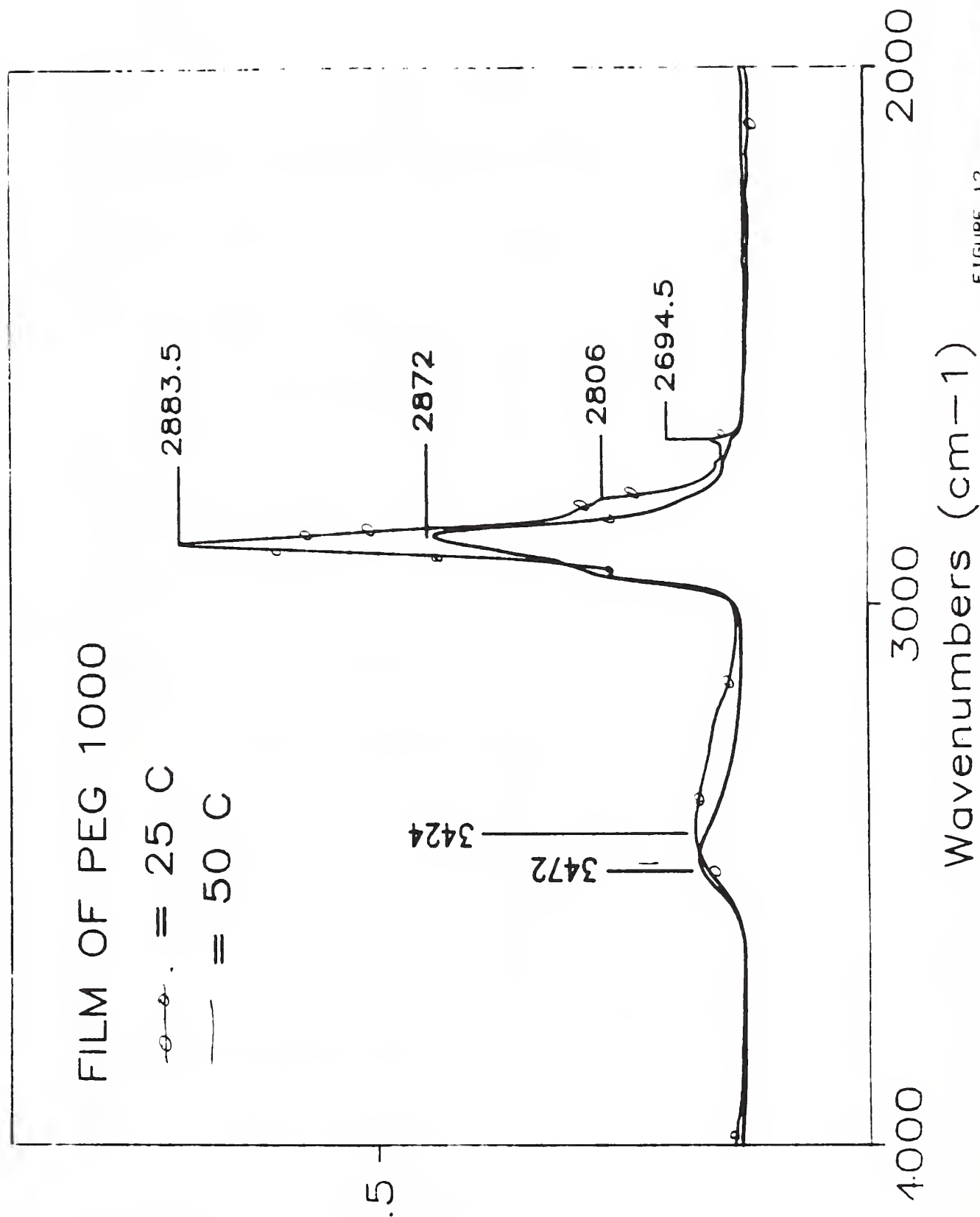


FIGURE 12

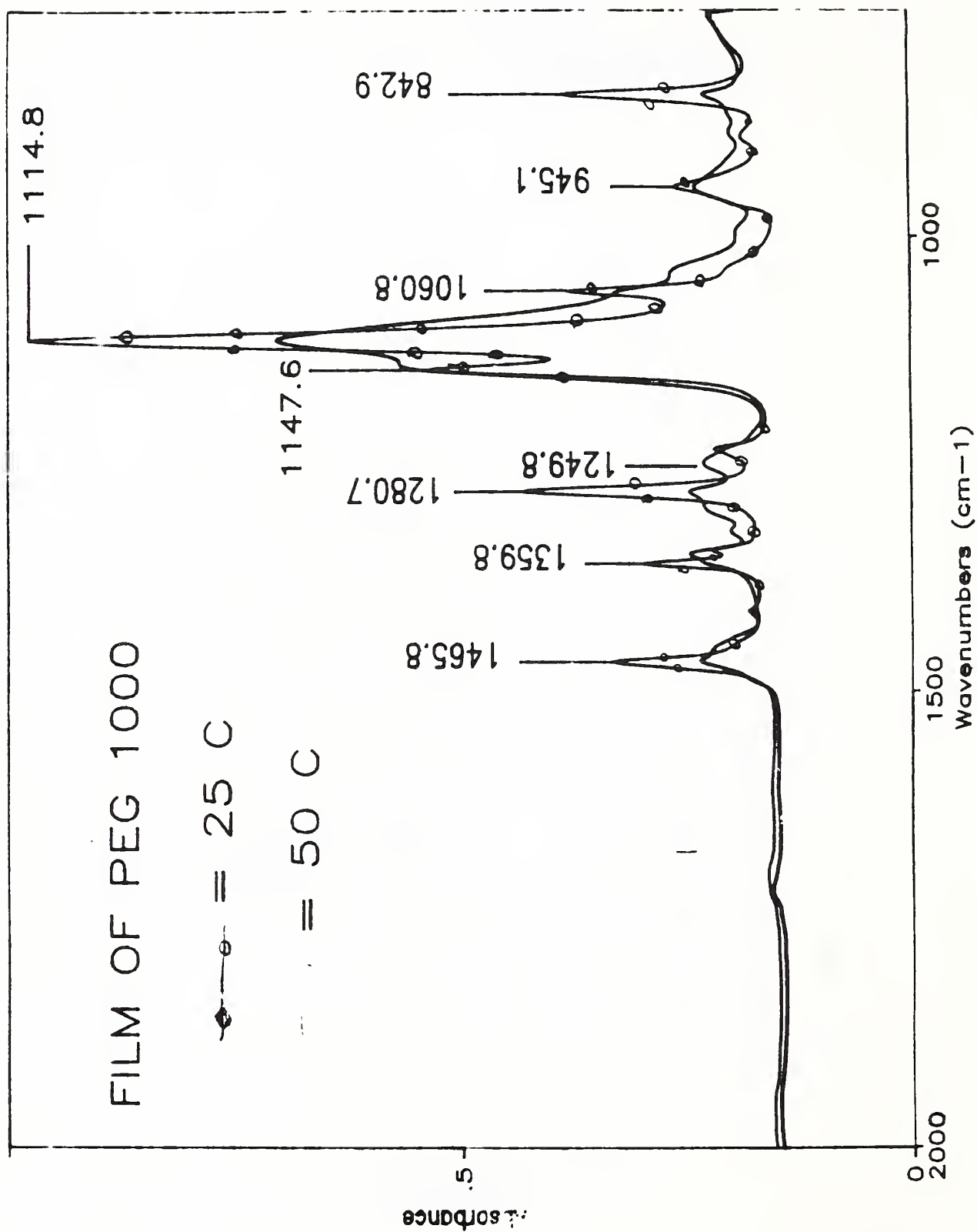


FIGURE 13

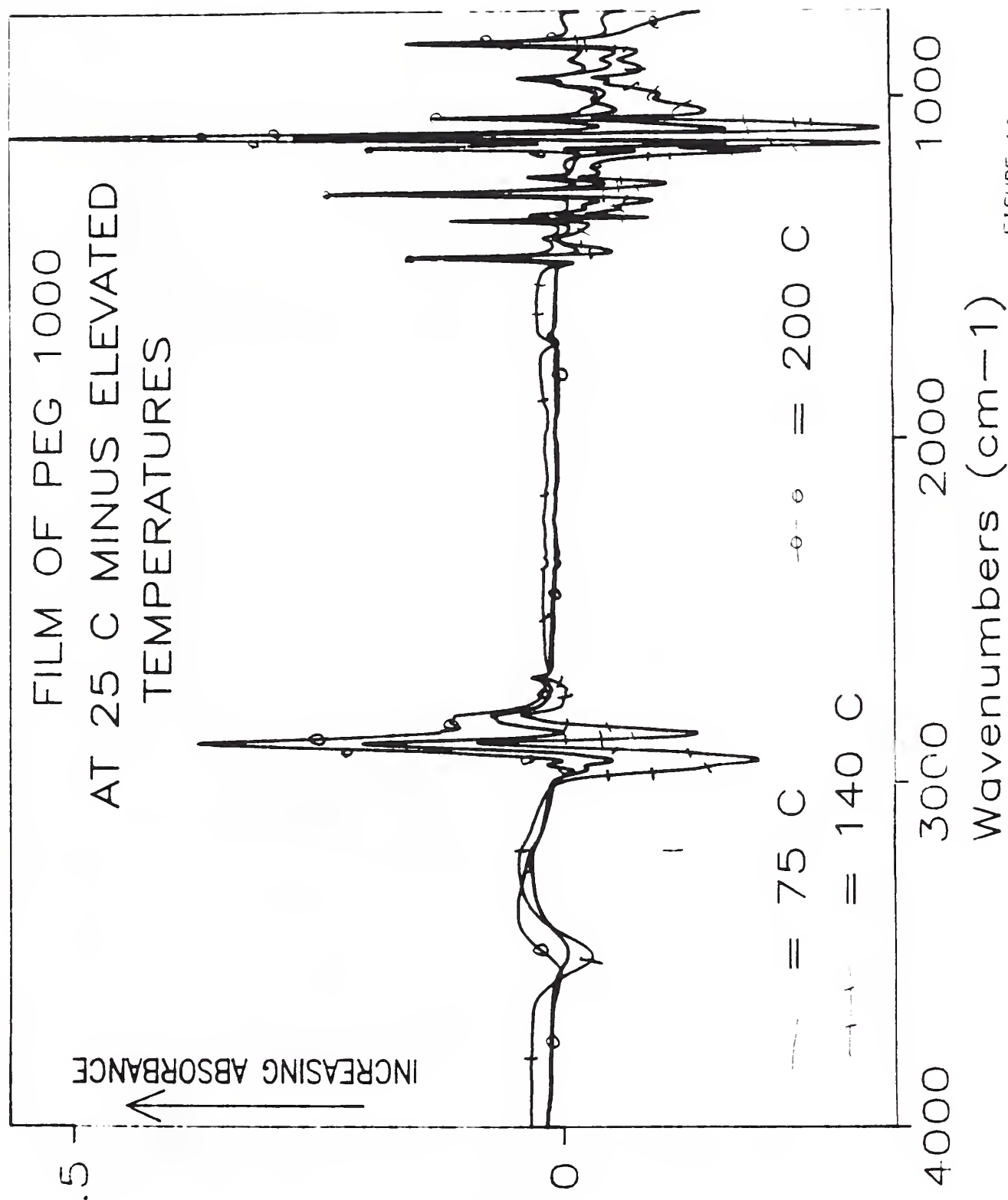


FIGURE 14

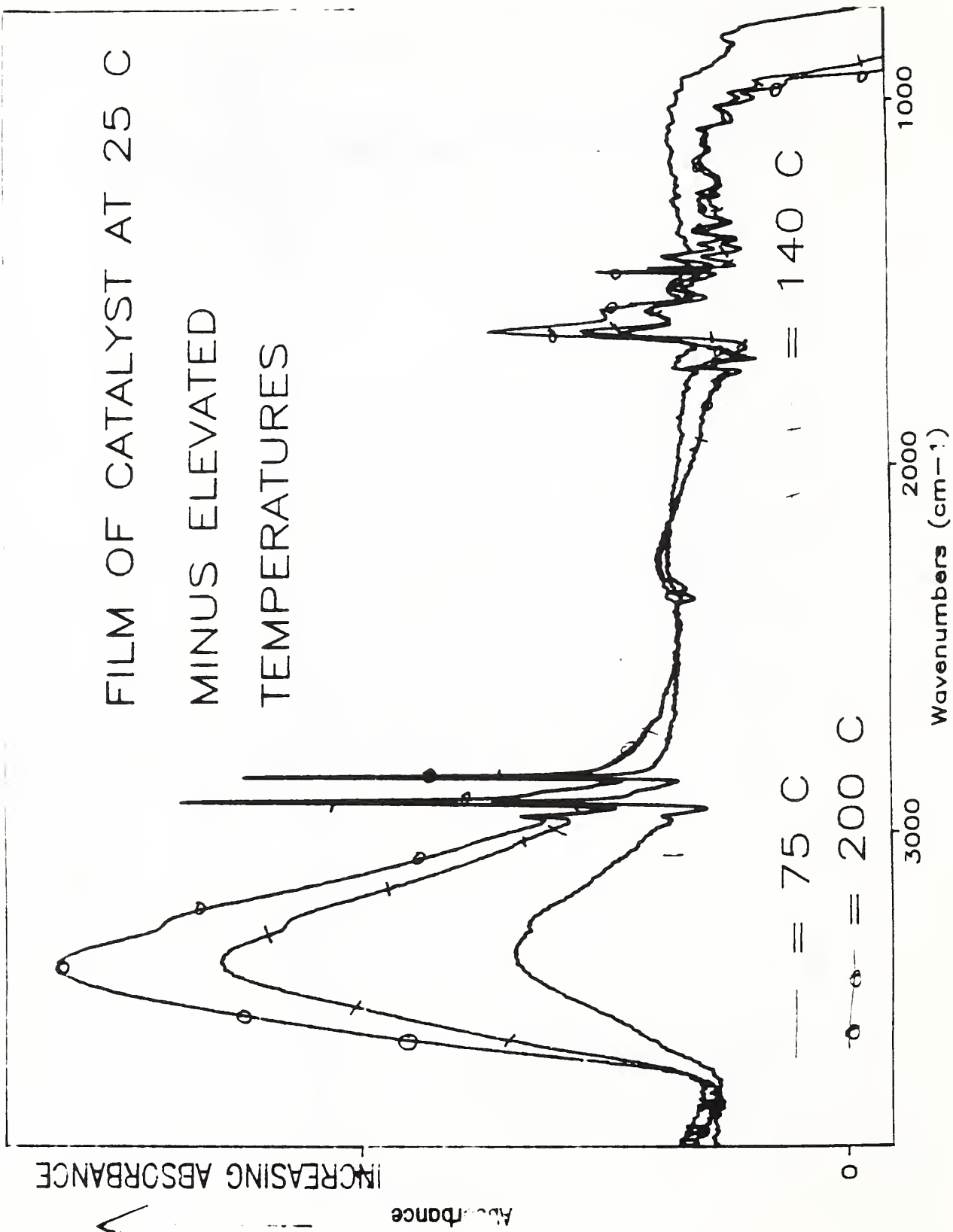


FIGURE 15

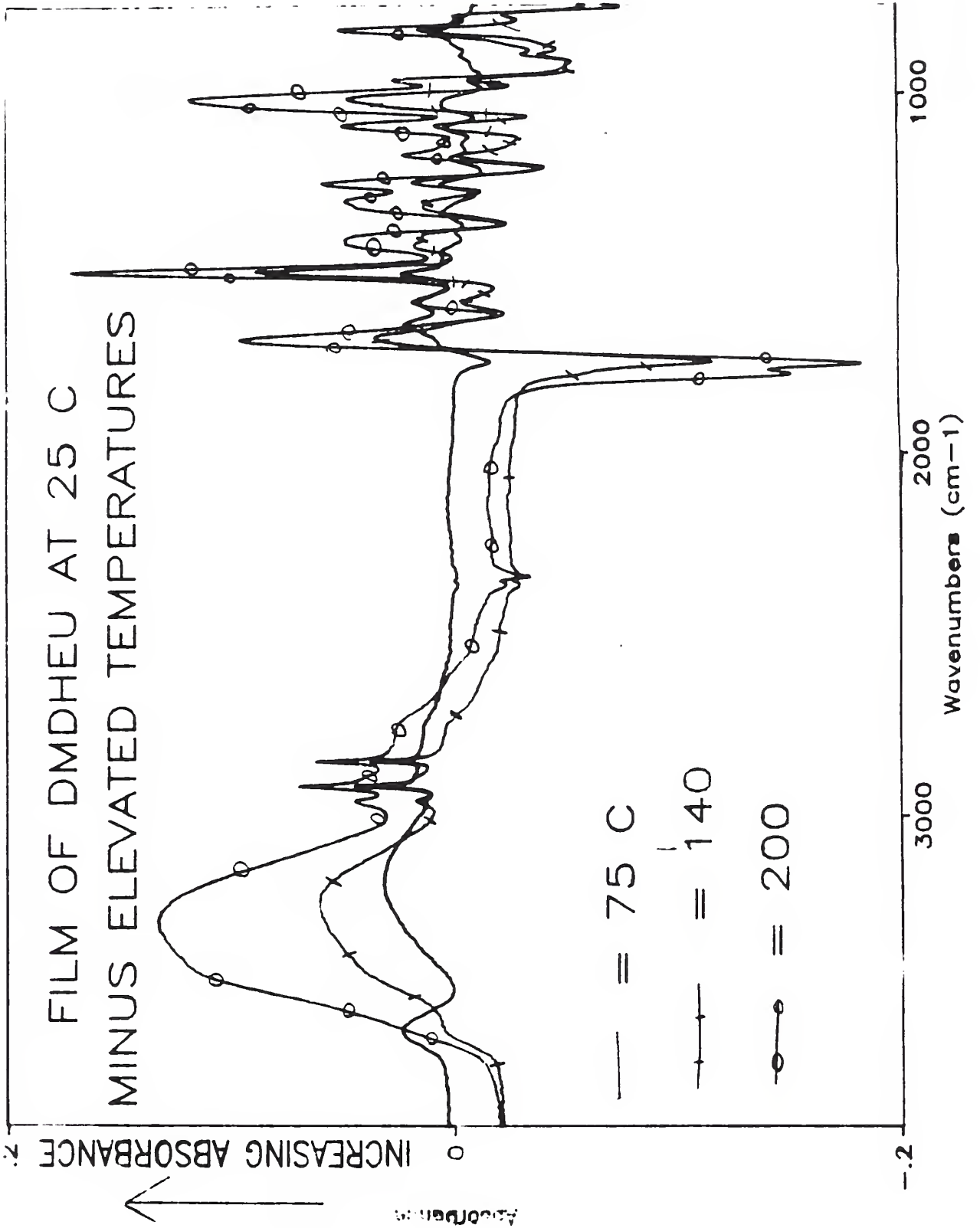
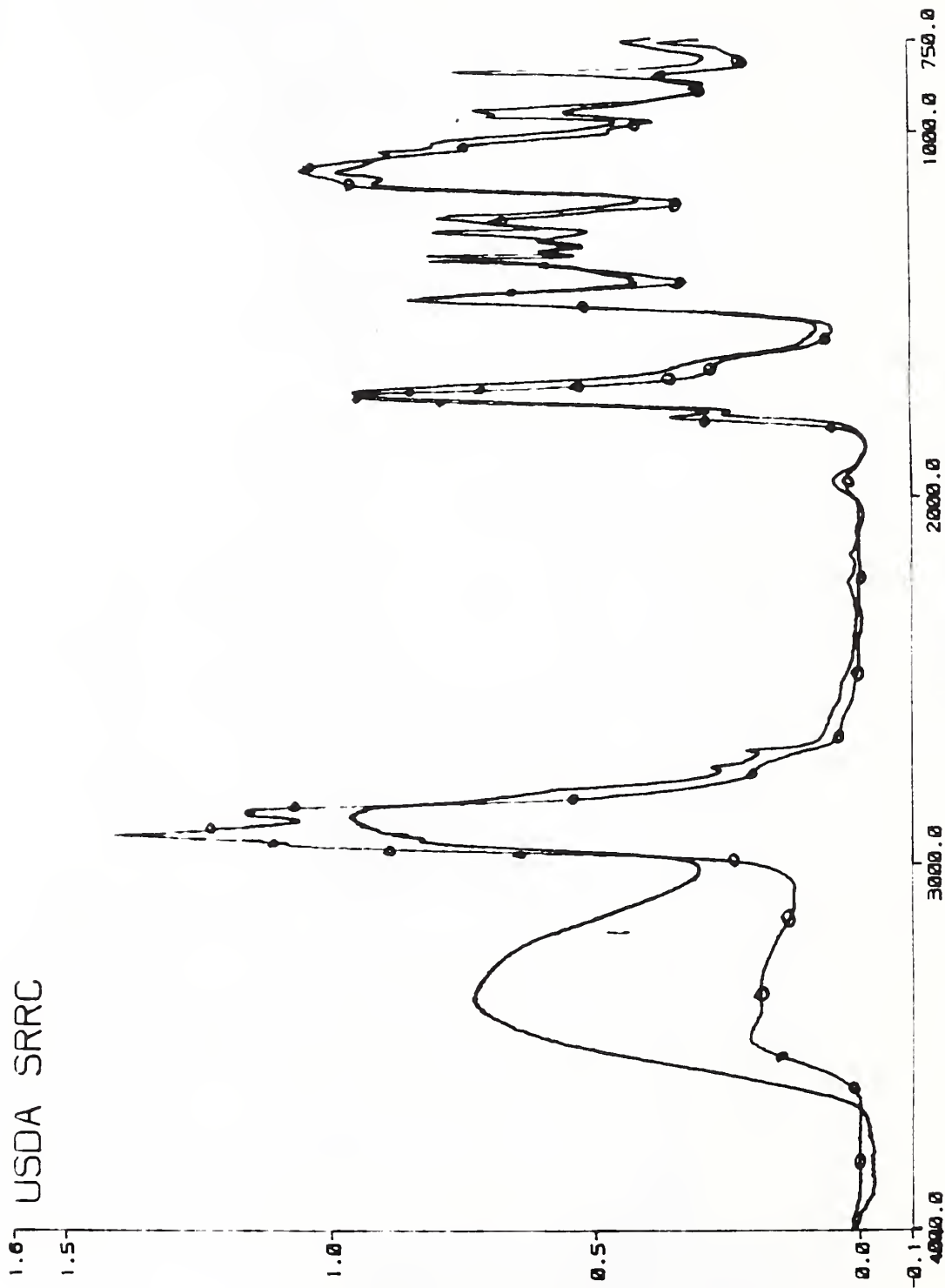


FIGURE 16

USDA SRRC



WAVENUMBERS

RES = 4.0

SAMP = V352

- = PES FILM AT 50 °C - = PES FILM AT 50 AFTER HEATING & RECOOL

SCANS = 64

FIGURE 17

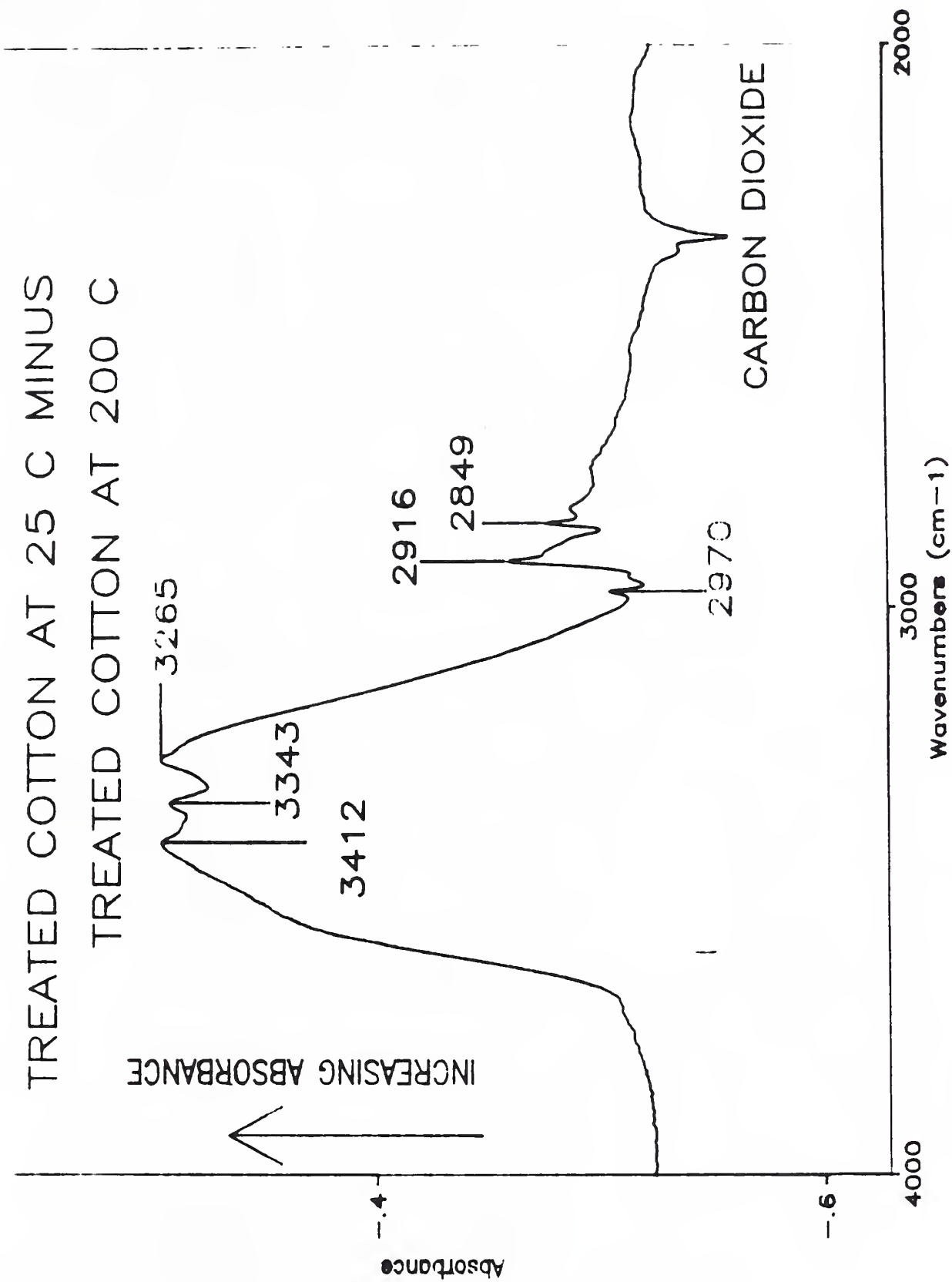


FIGURE 1B

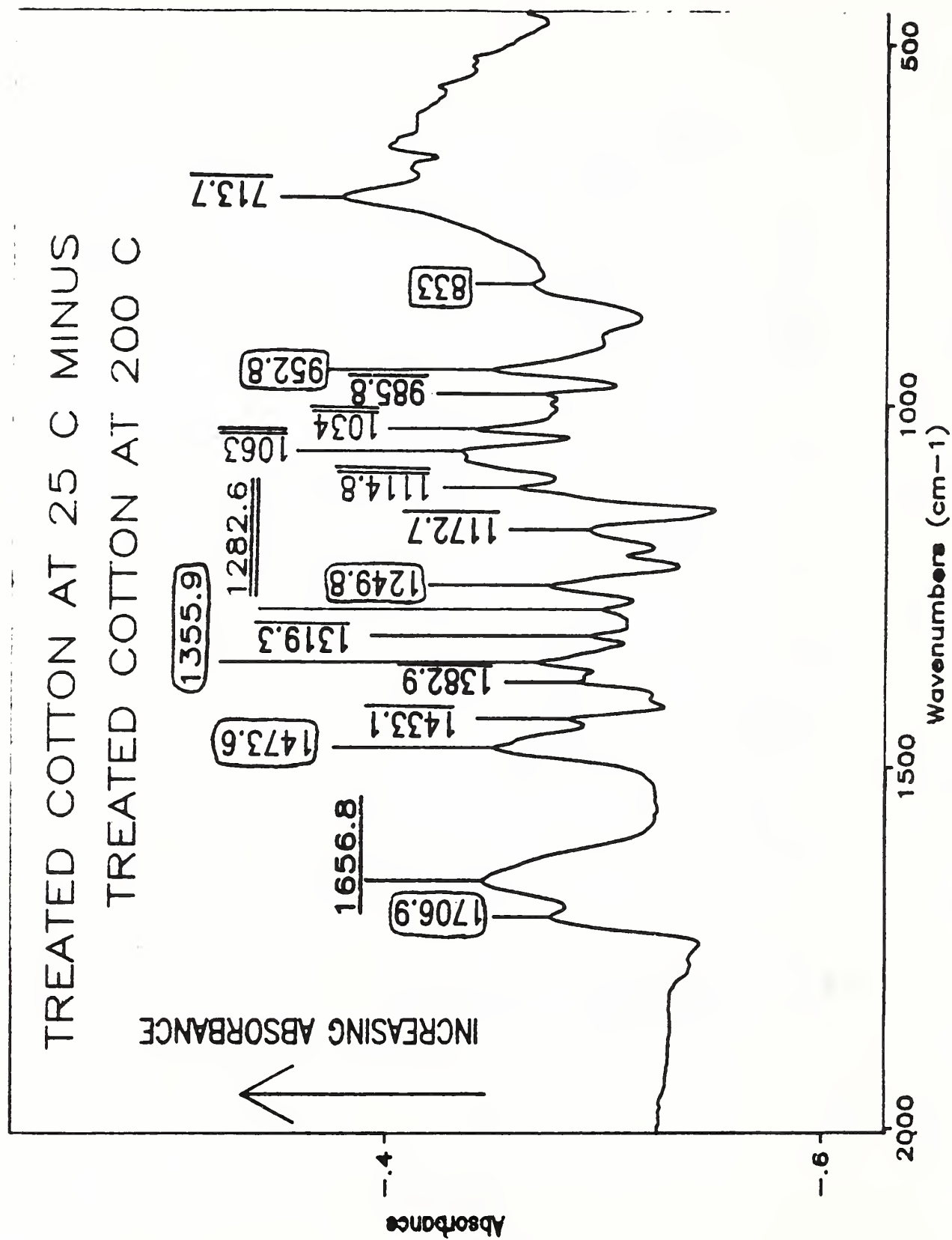


FIGURE 19

PEAK ASSIGNMENTS IN POLYETHYLENE GLYCOL SPECTRA

ASSIGNMENT	FREQUENCY (CM ⁻¹)	
	THIS STUDY	LITERATURE
OH STRETCHING	3427	3425
CH ₂ ASYMMETRIC STRETCH	2930	2930
CH ₂ SYMMETRIC STRETCH	2886	2875
CH ₂ SYMMETRIC STRETCH	2695	2730
CH ₂ BEND	1465.8	1460
CH ₂ WAG	1359.8	1352
CH ₂ WAG/TWIST	1344	1326
CH ₂ TWIST/WAG	1280.7	1296
CH ₂ TWIST	1242.1	1249
CH ₂ ROCKING/SKELETAL STRETCH	1147.6	1140
	1114.8	1107
TERMINAL -CH ₂ CH ₂ O-	1060.8	1070
STRETCH (CO)/CH ₂ ROCK	947	947
STRETCH (CO)/CH ₂ ROCK	845	843

FIGURE 20

Improving the Process for Treating Cotton Fabrics with Crosslinked Polyols

Joseph S. Bruno and Tyrone L. Vigo, SRRC
and John Turner, Cotton Incorporated

Addition of NaCl to pad bath solutions containing polyethylene glycol (50% PEG-1,000), crosslinking resin (11% DMDHEU) and mixed acid catalysts (3.3% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid) substantially increased the add on of 100% cotton fabrics (compared to fabrics treated with solutions without salt) when they were dried and cured. Fabrics comprised of synthetic fibers (e.g., polypropylene) and cotton blend fabrics containing 50% or more of synthetic fibers had only slightly higher weight gains when salt was in the pad bath solution. Concentrations of added NaCl were varied from 1 to 10% by weight and molar ratios of mixed acid catalysts were varied from 10/1 to 1/1 ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /citric acid). Concentrations of added NaCl and mixed catalyst ratios to obtain highest weight gains in the cotton fabrics were 5% and 5/1, respectively. Higher weight gains for cellulosic fabrics are attributed to reduction in penetration of the DMDHEU into the fiber due to an increase in the viscosity of the polyol solutions when NaCl is present, thus permitting optimum reaction of resin with the polyol at the fiber surface. The mode of action of the NaCl is also briefly discussed in relation to hypotheses that are consistent with fundamental polymer and physical chemistry.

Introduction

When polyols are applied on
a variety of fibrous substrates
then crosslinked,
the substrates become
thermally active.

Other Selected Fabric Properties

Resiliency (Durable Press)

Oily soil release

Improved wear resistance

Increase in moisture regain

Procedure for producing modified fabrics:

Pad/ Dry/ Cure Method

Solution:	50%	PEG 400 - 1500
	27.5%	Hylite LF (40%DMDHEU)
	3.3%	MgCl ₂ .6H ₂ O/Citric Acid 10/1
	19.2%	Water

Dry 60C for 6 min Cure 130C for 2 min

Process Wash

Certain Fabrics That are:

Tightly woven or have a high percentage of cellulosic fibers, will not benefit from this process because of very low add on of the polymer after washing.

DMDHEU (molecular diameter of 10 Å) penetrates into the cellulosic fiber.

Larger PEG (molecular diameter of 27 Å) stays on the surface.

There is substantially less reaction between the DMDHEU and the PEG because of this physical condition.

This talk describes:

1. A method for increasing the amount of resin available for reacting with the PEG.
2. Increasing the efficiency of the reaction between the resin and PEG.

100% Cotton Twill

	Wt. Gain %	%E	H cal/g	Break lb./in.	Stoll cycles	Moist. Regain
Treated	13.2	34	0.7	128	988	5.4
Untreated	-	-	0	183	520	5.1

50/50 Cotton/ Polyester Sheeting

	Wt. Gain %	%E	H cal/g	Break lb./in.	Stoll cycles	Moist. Regain
Treated	35.5	48	2.8	73	4979	12.7
Untreated	-	-	0	82	1520	2.9

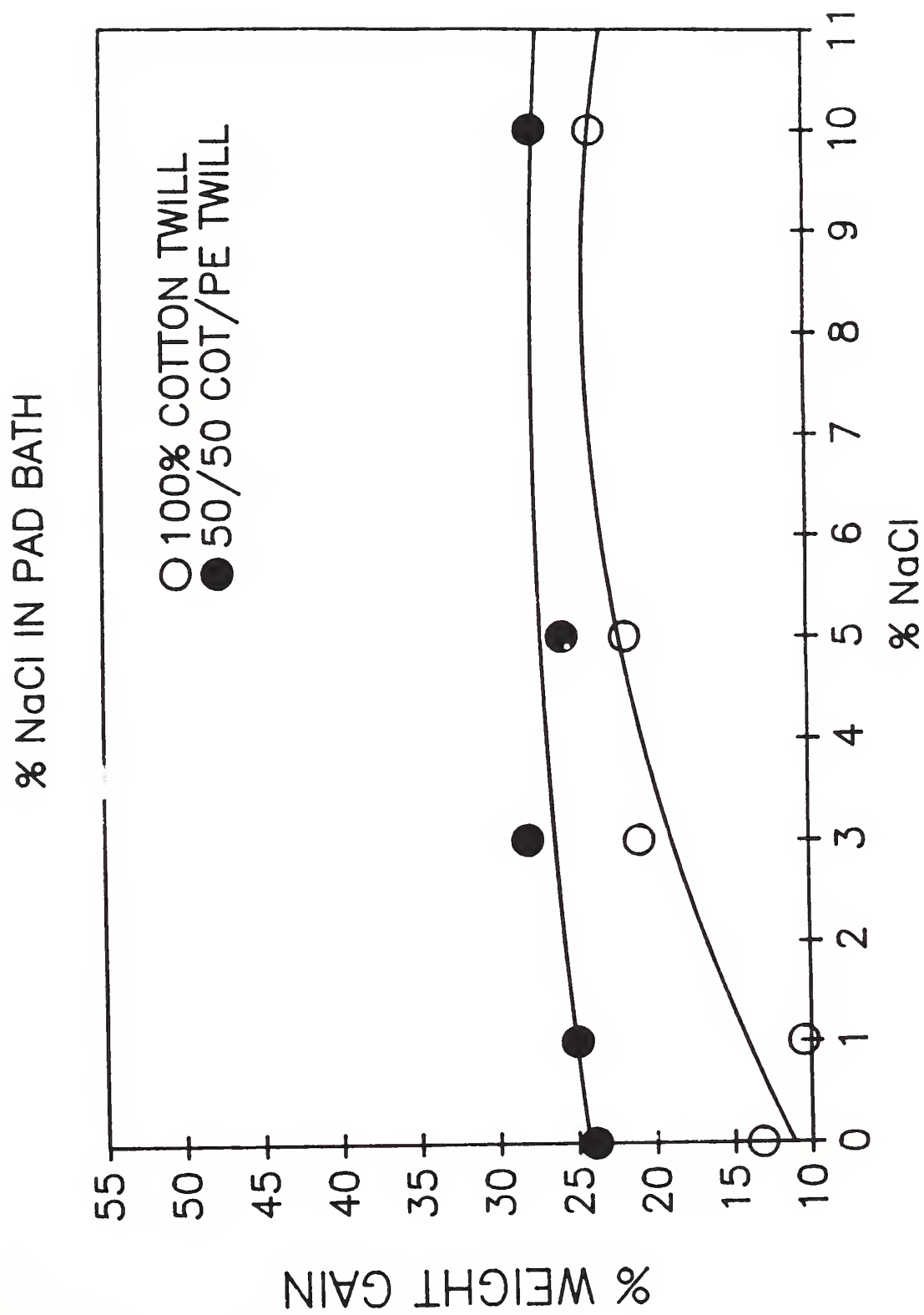
100% Polypropylene Taffeta

	Wt. Gain %	%E	H cal/g	Break lb./in.	Stoll cycles	Moist. Regain
Treated	43.6	46	3.8	147	4573	14.5
Untreated	-	-	0	157	4636	0.7

% Weight Gain VS % NaCl in Pad Bath

	0	1	3	5	10
100% Cotton P.C.	25.3	33.5	39.4	39.9	42.3
50/50 cot/PE	35.5	34.6	37.5	36.9	41.1
100% PP	43.6	46.8	47.9	47.0	44.7

FIGURE 1.



Some Possible Theoretical Reasons

Increase in viscosity caused by adding salt.

112 cps with 0 salt

160 cps with 5% salt

Reduction of the negative charge on the cellulosic fibers by altering surface sorption of fiber.

Reduction of the surface tension which reduces the wettability of fiber.

% Wt. Gain VS Molar Ratio of Catalyst

	10/1	5/1	3/1	2/1	1/1
100% C/PC	39.9	44.9	44.5	44.2	45.2
40/60 C/PET sheeting	29.8	36.9	35.6	35.2	35.5
100% PP Taffeta	47.0	50.9	49.9	46.5	49.7

Results With 5% NaCl and 5/1 Catalyst Ratio

	% Wt. Gain	H Cal/g	Break lb./in.	Stoll cycles	Moisture Regain	%Eff
100% Twill	29.2	2.4	130	1923	14.3	42
	13.2	0.7	128	988	5.4	34
100% PC	44.9	2.9	34	1311	19.8	48
	25.3	1.7	34	227	13.9	30

Results With 5% NaCl and 5/1 Catalyst Ratio

	% Wt. Gain	H Cal/g	Break lb./in.	Stoll cycles	Moisture Regain	%Eff
50/50 Sheet	43.1	2.8	71	5000+	22.3	56
	35.5	2.6	73	4979	12.7	48
100% PP	50.9	3.5	157	5000+	23.6	46
	43.6	3.8	147	4573	14.5	38

SUMMARY

The addition of 5% of NaCl and a catalyst ratio of 5/1 of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ /Citric Acid in the pad bath will improve the cross linked polyol add on to tightly woven highly cellulosic fabric thus improving thermal content, wear resistance and moisture regain.

Changing the catalyst ratio from 10/1 to 5/1 improves wear resistance and moisture content of highly synthetic fabrics.

Cationic Finishes for Garment Dyeing

Robert J. Harper, Jr.

Various approaches utilized in the past year to extend the choline system (process for dyeing smooth-dry cellulosic fabrics) were described. These included differential finishing of knits, procedures for producing pseudo-denims and generic denims, single side crosslinking, dyeing with rocks (wet with dye) in garment dyeing machines, and development of markers for print applications with the choline system.

A second phase of this presentation covered the response of two types of cationic fabric to various dye types and procedures. One type was produced using a cationic polyacrylate in the finish. The other used a small molecule to react to the crosslinking agent to graft this molecule to the cellulose. In general, fabrics treated with cationic polyacrylate and crosslinking agent were dyeable with certain types of pigment dyes, whereas the choline system responded better to anionic dyes.

Pigment dyed cellulose fabrics showed excellent lightfastness and fair durability to laundering. Blend fabrics treated with crosslinking agent and cationic polyacrylate could be uniformly dyed subsequent to finishing, whereas the choline system only imparts a cationic character to the cellulose component of a blend.

Various aspects of single side finishing were discussed. Numerous dyed samples were shown to demonstrate the versatility of the choline system and the utility of single side finishing for garment dyers.

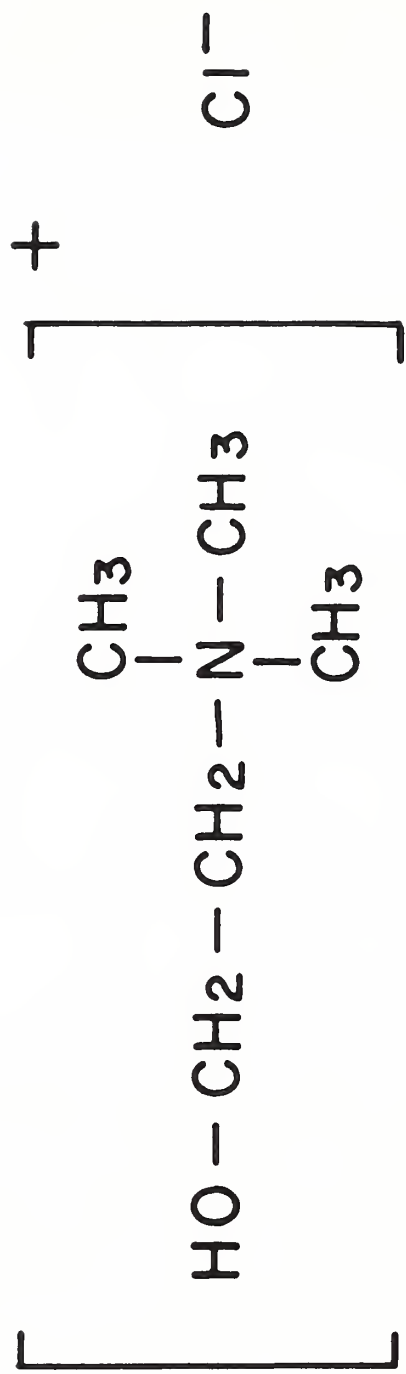
DP FINISHING

1. Extension of choline system
2. Cationic polyacrylates
3. Single side crosslinking for dyeability
4. Non-formaldehyde finishing

COTTON + X-LINKER + QUATERNARY



X-LINKED COTTON
WITH GRAFTED QUAT



CHOLINE CHLORIDE

EXTENSION OF THE CHOLINE SYSTEM

1. Differential finishing of knits
2. Production of pseudodenims
3. Single-side crosslinking
4. Generic denims

FINISHING

<u>FABRIC</u>	<u>CROSSLINKER</u>	<u>POLYACRYLATE</u>	<u>DP</u>
M Cotton	5% DMDHEU	5% B	3.1
M Cotton	5% DMDHEU	5% A	2.7
NM Cotton	5% 3-ACD	5% B	3.2
NM Cotton	5% 3-ACD	5% A	2.7
50C/50P	5%DMDHEU	5% B	3.6

K/S VALUES OF DYED FABRICS

<u>FABRIC</u>	<u>CATIONIC</u>	<u>REACTIVE RED 40</u>	<u>ACID ORANGE 74</u>	<u>BLUE PIGMENT</u>
NM Cotton	5% Poly B	1.0	3.4	11.5
M Cotton	5% Poly B	1.0	3.8	11.8
M Cotton	6% CC	18.6	16.7	1.1
50C/50P	5% Poly B	0.9	4.2	15.1
M Cotton	none	0.0	0.2	1.0

K/S VALUES OF DYED FABRICS

<u>FABRIC</u>	<u>CATIONIC</u>	<u>PIGMENT</u>		
		<u>GREEN</u>	<u>RED</u>	<u>YELLOW</u>
NM Cotton	5% Poly B	8.0	8.0	3.9
M Cotton	5% Poly B	9.0	8.4	4.7
M Cotton	6% CC	1.6	0.2	0.7
50C/50P	5% Poly B	10.1	8.6	6.2
M Cotton	none	0.4	0.3	0.1

K/S OF 50C/50P; ACID VS ALKALINE

=====

<u>% POLY B</u>	<u>METROPAD BLUE</u>	<u>SPEEDYE GREEN</u>
2	12.5	7.1
3	11.2	8.6
5	12.9	9.7
		6.7
		7.4
		8.0
		4.1
		4.8
		5.3

1

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Dye Bath pH	4.1	9.0	3.8	9.2
-------------	-----	-----	-----	-----

K/S VALUES OF PIGMENT DYED FABRIC

FABRIC	LAUNDERINGS			
	DYE	1	10	25
NM Cotton	Green	8.3	4.4	4.1
M Cotton	Green	8.5	4.1	4.1
50C/50P	Green	10.1	4.8	4.7
NM Cotton	Blue	11.5	4.8	4.4
M Cotton	Blue	10.4	5.2	4.7
50C/50P	Blue	14.2	5.5	4.7

LAUNDERING OF PIGMENT DYED 50C/50P FABRIC

LAUNDERINGS

0	5	10	25
---	---	----	----

% POLY	DYE pH	DYE	K/S VALUES
--------	--------	-----	------------

2	4	Green	7.4	6.5	5.9	5.7
5	4	Green	8.0	6.8	6.7	6.0
2	9	Green	3.8	3.6	3.6	3.4
5	9	Green	5.2	4.8	4.9	4.8

LAUNDERING OF PIGMENT DYED 50C/50P FABRIC

% POLY	DYE pH	DYE	LAUNDERINGS			
			0	1	10	25
			K/S VALUES			
2	4	Blue	7.4	7.1	6.2	5.9
3	4	Blue	8.3	8.6	7.5	7.1
5	4	Blue	9.0	9.0	8.8	8.1

LIGHTFASTNESS --- XENON ARC

	<u>YELLOW</u>		<u>GREEN</u>	
<u>FABRIC</u>	<u>20 hr</u>	<u>80 hr</u>	<u>20 hr</u>	<u>80 hr</u>
M Cotton	5.0	5.0	5.0	5.0
NM Cotton	5.0	5.0	5.0	5.0
50C/50P	5.0	5.0	5.0	5.0

LIGHTFASTNESS --- XENON ARC

	<u>RED</u>		<u>BLUE</u>	
<u>FABRIC</u>	<u>20 hr</u>	<u>80 hr</u>	<u>20 hr</u>	<u>80 hr</u>
M Cotton	4.5	4.5	5.0	5.0
NM Cotton	5.0	4.5	5.0	5.0
50C/50P	5.0	5.0	4.5	4.5

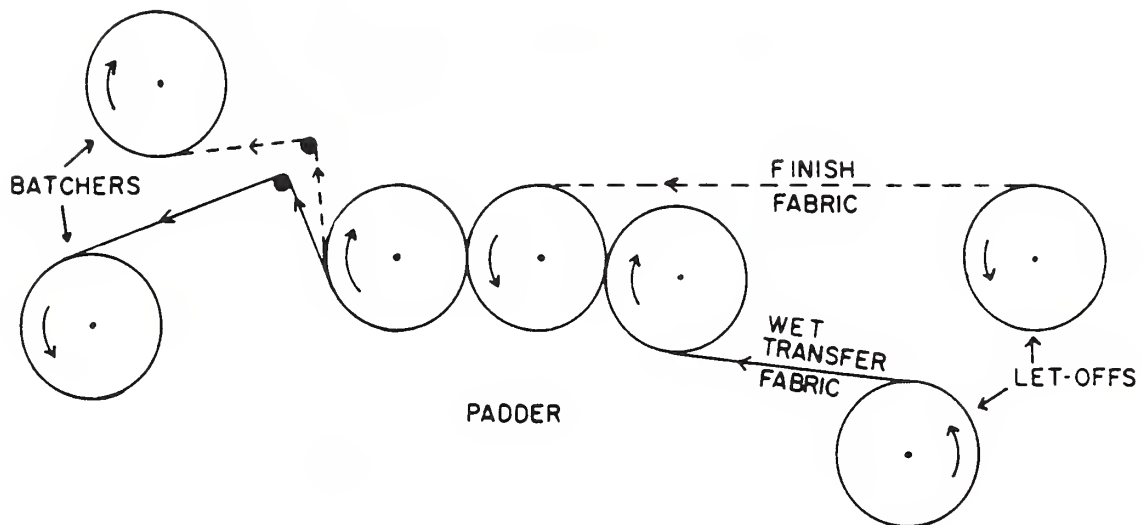
DYEING WITH PIGMENTS

1. Dyeable smooth-dry fabrics
2. Yields bright colors
3. Even dyeing of blends
4. Excellent lightfastness
5. Contrasts with small grafts
6. Durable to laundering -- fair to good
7. Vulnerable to edge abrasion

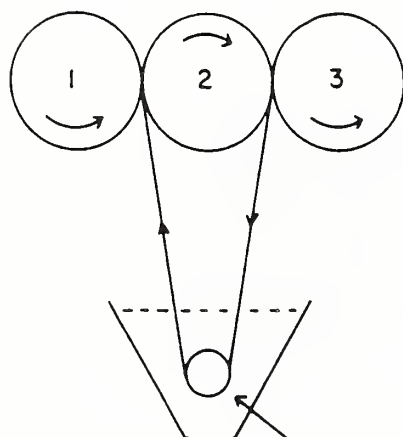
SINGLE-SIDED CROSSLINKING

1. Loop transfer, pad transfer
2. Foam finishing
3. Coating treatments
4. Reverse side - catalyst poison
5. Back or face crosslinking
6. Partial face crosslinking

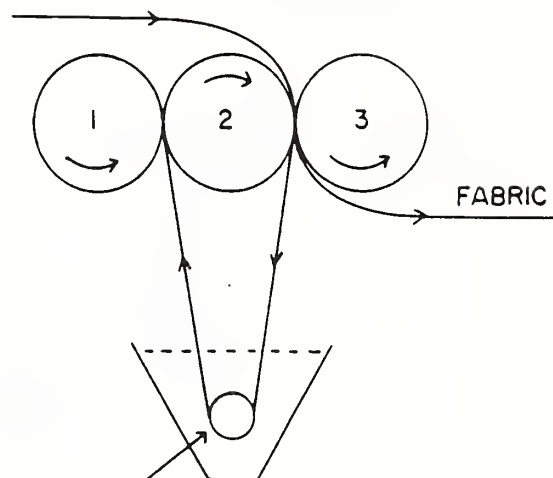
TRANSFER TECHNIQUE



(A)
THREE-ROLL PAD
WITH TRANSFER LOOP



(B)
LOOP TRANSFER
PROCESS



AGENT
SOLUTION

Single Side Crosslinking Via Foam Finishing

Allan H. Lambert and Robert J. Harper, Jr.

Single side, low add-on application of foam containing crosslinker to cotton fabrics provides an approach for a smooth-drying dyeable fabric. Such a fabric has potential for garment dyeing application. Two procedures were tested. Foam containing a crosslinker and a reactive additive was applied to the face of the fabric while the back side was untreated. This allowed dyeing the face side only by use of a modified dye procedure. This procedure was compared with applying foam containing a conventional crosslinker system to the back side of the fabric. Dyeing the face side of this fabric with conventional cotton dye procedures was then possible.

Post dyeing color differences of the fabric's face and back potentially opens the way to stone washing or acid washing after drying. Foam application techniques used to accomplish single side crosslinking are described as well as the dyeing and smooth-dry characteristics of said fabric.

SINGLE-SIDE CROSSLINKING VIA FOAM FINISHING TO PRODUCE GARMENT DYEABLE COTTON FABRICS

=====

PURPOSE:

1. A smooth dry fabric ready to dye
2. Less dye.
3. Improve strength properties
by crosslinking only one
side.
4. Fabric amenable to stone washing.

FORMULATIONS

1. 12-20% DMDHEU
2. 5.4-6% catalyst ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or glycolic acid)
3. 1% P.E. softener
4. 0-19% choline chloride (CC) or triethanolamine (TEA)
5. 2% non-ionic surfactant

PROCEDURE

=====

1. Foam applied to one side at a foam rate of 110 g/min with a blow ratio of 30/1. Foamer speed was 900 RPM. Fabric velocity was adjusted to give desired WPU (4-14%).
2. Dried at 190°F for 2 minutes.
3. Cured at 320°F for 4 minutes.
4. Washed and tumble dried.
5. Fabric evaluated.

DYEING

Fabric dyed with C.I. Reactive 29. If the formulation contained CC or TEA (applied to face side), fabric was dyed under acid conditions. Otherwise (applied to back side), fabric was dyed under alkaline conditions.

FABRIC EVALUATION

=====

1. Dyeability of face and back --
 - a) $K/S = (1-R)^2 / 2R$
2. DP and WRA
3. Break and tear strength

**Table I: Dyeability of Fabrics Dyed with Reactive
Blue 29 Under Acid Conditions**

TREATMENT ¹	% WPU	K/S ²	
		FACE	BACK
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	14	8.29	0.19
12% DMDHEU 16% CC 5% MgCl ₂ ·6H ₂ O	10	5.44	0.21
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	10	6.08	0.17
13% DMDHEU 17% CC 5.4% MgCl ₂ ·6H ₂ O	7	4.60	0.13
13% DMDHEU 15% TEA 5.4% MgCl ₂ ·6H ₂ O	7	9.89	0.15
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	4	8.83	0.25
Untreated Fabric	—	0.11	0.13

1) Treatment applied to face side of fabric; dyed by procedure A.

2) Wavelength was 598 nm.

**Table II: Dyeability of Fabric Dyed with Reactive
Blue 29 Under Alkaline Conditions**

TREATMENT ¹	%WPU	K/S ²	
		FACE	BACK
20% DMDHEU 6% MgCl ₂ ·6H ₂ O	14	4.99	0.54
16% DMDHEU 6% Glycolic Acid	12	4.73	1.04
Untreated Fabric	--	5.70	5.44

1) Treatment applied on back side of fabric; dyed by procedure B.

2) Wavelength was 598 nm.

Table III: K/S Values for Dyed Fabrics¹

DYE	K/S	
	FACE	BACK
Reactive Orange 16	12.53	0.16
Reactive Blue 184	18.24	0.37
Reactive Blue 19	9.89	0.23
Acid Orange 74	7.36	0.37
Intracron Red VS-4BL	12.53	0.22

- 1) Dyed by procedure A; 10% WPU; 12% DMDHEU, 16% CC, 5% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ applied to face side.

Table IV: Smooth Dry Performance of Fabrics Treated with
Reactive Additive on Face Side

=====				
WRINKLE RECOVERY ANGLE ¹				
W+F)				
TREATMENT	% WPU	CONDITIONED	WET	DP RATING
-----	-----	-----	-----	-----
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	14	165	187	3.4
12% DMDHEU 16% CC 5% MgCl ₂ ·6H ₂ O	10	141	173	3.0
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	10	156	192	3.0
13% DMDHEU 17% CC 5.4% MgCl ₂ ·6H ₂ O	7	149	173	3.0
13% DMDHEU 15% TEA 5.4% MgCl ₂ ·6H ₂ O	7	149	173	3.0
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	4	148	172	3.0
Untreated Fabric	---	162	161	2.5
=====				

1) Wrinkle recovery angle given in degrees.

Table V: Smooth Dry Performance of Fabric
Treated on Back Side

WRINKLE RECOVERY ANGLE ¹ (W+F)				
TREATMENT	%WPU	CONDITIONED	WET	DP RATING
20% DMDHEU 6% MgCl ₂ ·6H ₂ O	14	203	189	3.5
16% DMDHEU 6% Glycolic Acid	12	164	162	3.1
Untreated Fabric	---	162	161	2.5

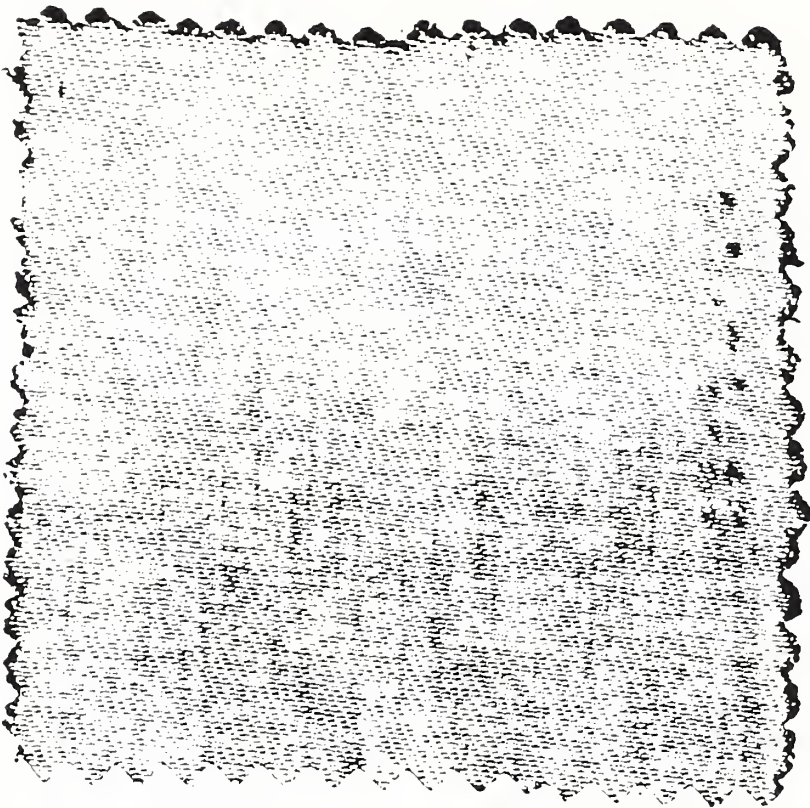
1) Wrinkle recovery angle given in degrees.

**Table VI: Effect of Treatments on Strength Properties of
Fabric Treated with Reactive Additive on
Face Side**

TREATMENT	% WPU	% RETENTION OF TEAR STRENGTH		% RETENTION OF BREAK STRENGTH	
		WARP	FILL	WARP	FILL
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	14	38.5	65.2	65.4	74.8
12% DMDHEU 16% CC 5% MgCl ₂ ·6H ₂ O	10	55.8	76.4	72.8	79.4
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	10	51.0	73.0	68.6	70.6
13% DMDHEU 17% CC 5.4% MgCl ₂ ·6H ₂ O	7	56.3	70.8	88.1	91.7
13% DMDHEU 15% TEA 5.4% MgCl ₂ ·6H ₂ O	7	47.1	68.6	70.4	72.81
16% DMDHEU 19% CC 6% MgCl ₂ ·6H ₂ O	4	76	102	100	100
Untreated Fabric	---	100	100	100	100

**Table VII: Effect of Treatments on Strength Properties of
Fabric Treated on the Back Side**

TREATMENT	%WPU	% RETENTION OF TEAR STRENGTH		% RETENTION OF BREAK STRENGTH	
		WARP	FILL	WARP	FILL
16% DMDHEU 6% MgCl ₂ ·6H ₂ O	14	41.4	31.2	69.2	43.4
12% DMDHEU 6% Glycolic Acid	12	64.9	52.8	92.6	78.9
Untreated Fabric	---	100	100	100	100



BACK

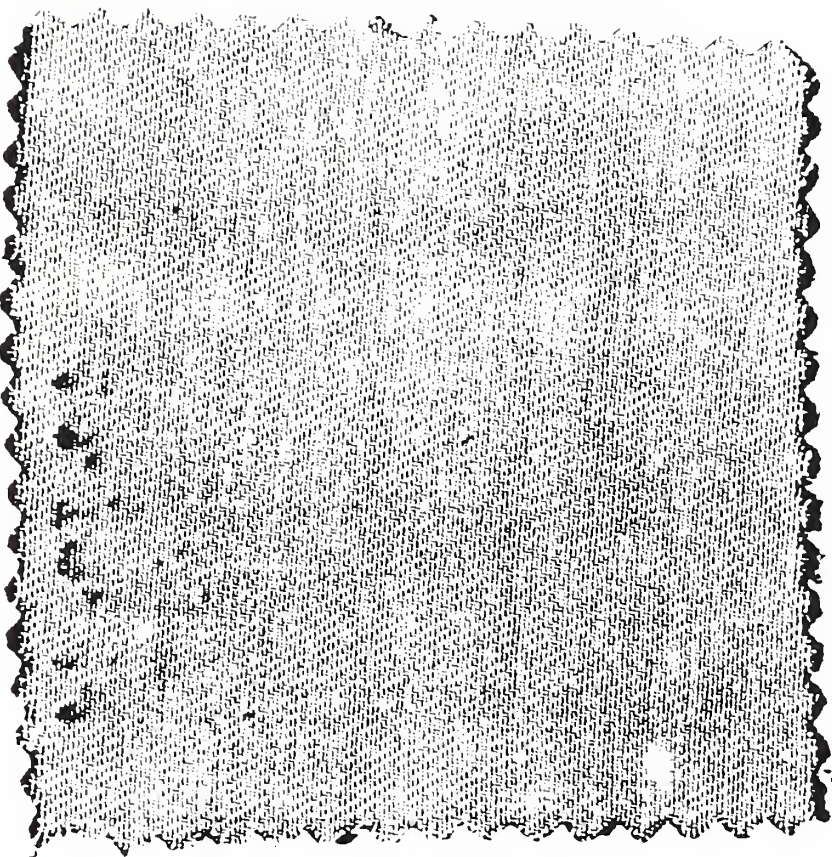


FACE

Fig 1 : Treatment applied & too late



FACE



BACK

Fig 2 "Treatment applied to Backboard"

EFFECTS OF MERCERIZATION AND REDUCED WET PICKUP
ON PROPERTIES OF FABRICS CROSSLINKED WITH BTCA

Cletus E. Morris

This presentation is a preliminary version of a paper to be presented at a meeting of the American Chemical Society (#1). It reports results of applying variations that have been tried for improving DMDHEU finishes -- low wet pickup application of the agent and prior mercerization of the fabric -- to treatments that have been reported (#2) to give good results in no-formaldehyde crosslinking of cotton fabric with 1,2,3,4-butanetetracarboxylic acid (BTCA).

BTCA was applied to mercerized and unmercerized cotton fabrics (#3) via a conventional pad-dry-cure process (#4) at the same application level owf as in the cited papers, but at somewhat lower wet pickup (about 90% for printcloth). Sodium hypophosphite or monosodium phosphate was included as a co-reactant catalyst. BTCA was applied at a similar level at reduced wet pickup by loop transfer padding followed by the same drying and curing steps (#5). Because of BTCA's limited solubility, it was found advisable to limit its concentration in the bath to about 18%.

When unmercerized and mercerized fabrics were given identical treatments, using the same pad bath, the DP ratings always were lower for the mercerized fabric (#6-7). The mercerized fabrics tended to have better strength retention after the crosslinking.

When fabrics were given conventional and low wet pickup treatments at similar application levels owf, the low wet pickup treatments generally led to higher DP ratings -- especially for the unmercerized fabrics -- and to about the same strength retention as for the conventional treatments (#8-11). For the low wet pickup treatments, the DP ratings remained practically constant over a fairly wide range of application levels.

Replacing the polyethylene softener normally used in these treatments with nonionic or cationic silicones led to higher wrinkle recovery angles, but the DP ratings either were essentially unchanged or were slightly lower (#12).

EFFECTS OF MERCERIZATION AND REDUCED WET
PICKUP ON PROPERTIES OF COTTON FABRICS
CROSSLINKED WITH A TETRACARBOXYLIC ACID

CLETUS E. MORRIS
and
ROBERT J. HARPER, JR.

CELL #43, 198th American Chemical Society
National Meeting, Miami Beach

Transparency 1

Welch, Text. Res. J. **58**, 480 (1988)

Welch and Andrews, Book Pap., AATCC Int.
Conf. 1988, 85

Welch and Andrews, Text. Chem. Color.
21(2), 13 (1989)

Transparency 2

COTTON FABRICS

PRINCLOTH, 3.3 oz/yd²

SAME, CAUSTIC-MERCERIZED

TWILL, 6.8 oz/yd²

SAME, CAUSTIC-MERCERIZED

Transparency 3

CONVENTIONAL APPLICATION OF BTCA

(1,2,3,4-BUTANETETRACARBOXYLIC ACID)

PAD BATH

7.2-10.8% BTCA

SODIUM HYPOPHOSPHITE OR MONOSODIUM

PHOSPHATE, 1.14 MOLES/MOLE OF BTCA

1% (SOLIDS) NONIONIC POLYETHYLENE

DRY: 5 MIN. AT 85°C

CURE: 90 SEC. AT 180°C

MACHINE WASH

TUMBLE DRY

Transparency 4

LOOP TRANSFER APPLICATION

BATH

18-20% BTCA

OTHER COMPONENTS IN SAME PROPORTION TO

BTCA AS IN CONVENTIONAL APPLICATION

EXCEPTION: WITH NaH_2PO_4 AS

CATALYST, SOFTENER APPLIED

AFTER CURE (PADDED THROUGH

1% EMULSION AND DRIED)

2-5 PASSES

WET PICKUP 31-58%

DRY AND CURE AS FOR CONVENTIONAL APPLICATION

Transparency 5

PRINTCLOTH
EFFECTS OF PRIOR MERCERIZATION

MERCER- IZED	CTLYST	% WPU	% BTCA owf	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
NO	-	-	-	1.2	195	1	100	100
YES	-	-	-	1.1	182	1	100	100
NO	NaH ₂ PO ₂	92	7.5	4.0	287	0	51	45
YES	NaH ₂ PO ₂	87	7.1	3.6	280	19	74	78
NO	NaH ₂ PO ₄	91	7.5	3.6	281	12	43	34
YES	NaH ₂ PO ₄	84	6.9	2.8	261	10	28	28
NO	NaH ₂ PO ₂	38	7.6	4.5	297	14	50	44
YES	NaH ₂ PO ₂	31	6.2	3.3	288	9	68	75
NO	NaH ₂ PO ₄	41	8.2	3.6	288	14	46	49
YES	NaH ₂ PO ₄	40	7.9	3.2	271	13	67	79

Transparency 6

TWILL
EFFECTS OF PRIOR MERCERIZATION

MERCER- IZED	CTLYST	% WPU	% BTCA owf	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
NO	-	-	-	1.5	165	2	100	100
YES	-	-	-	1.3	163	2	100	100
NO	NaH ₂ PO ₂	71	7.6	3.9	252	24	66	41
YES	NaH ₂ PO ₂	67	7.2	3.4	272	19	65	84
NO	NaH ₂ PO ₄	71	7.7	3.1	233	22	62	41
YES	NaH ₂ PO ₄	68	7.3	2.9	253	17	33	49
NO	NaH ₂ PO ₂	40	7.3	4.2	245	16	65	40
YES	NaH ₂ PO ₂	40	7.1	4.0	229	20	69	80
NO	NaH ₂ PO ₄	34	6.1	3.9	247	18	62	-
YES	NaH ₂ PO ₄	38	6.8	3.6	263	15	65	81
NO	NaH ₂ PO ₂	41	8.2	4.3	237	22	69	40
YES	NaH ₂ PO ₂	46	9.2	3.9	282	25	65	35
NO	NaH ₂ PO ₄	50	10.0	4.0	258	25	61	41
YES	NaH ₂ PO ₄	58	11.6	3.6	265	25	66	78

Transparency 7

UNMERCERIZED PRINTCLOTH

CTLYST	% WPU	% BTCA owf	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
-	-	-	1.2	195	1	100	100
NONE	86	7.0	2.3	228	5	48	59
NONE	39	7.8	2.2	237	5	53	73
NaH ₂ PO ₂	34	6.1	4.3	293	10	50	46
NaH ₂ PO ₂	92	7.5	4.0	287	0	51	45
NaH ₂ PO ₂	38	7.6	4.5	297	14	50	44
NaH ₂ PO ₄	32	5.8	3.7	277	8	41	45
NaH ₂ PO ₄	91	7.5	3.6	281	12	43	34
NaH ₂ PO ₄	41	8.2	3.6	288	14	46	49

Transparency 8

MERCERIZED PRINTCLOTH

CTLYST	% WPU	% BTCA owf	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
-	-	-	1.1	182	1	100	100
NONE	80	6.6	1.7	235	4	49	94
NONE	34	6.9	2.0	229	4	47	89
NaH ₂ PO ₂	80	5.8	3.4	250	10	70	79
NaH ₂ PO ₂	31	6.2	3.3	288	9	68	75
NaH ₂ PO ₂	87	7.1	3.6	280	19	74	78
NaH ₂ PO ₄	84	6.9	2.8	261	10	28	28
NaH ₂ PO ₄	40	7.9	3.2	271	13	67	79
NaH ₂ PO ₄	83	8.0	3.5	254	11	64	77

Transparency 9

UNMERCERIZED TWILL

CTLYST	% WPU	% BTCA owf	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
-	-	-	1.5	165	2	100	100
NONE	67	7.2	2.1	188	13	62	51
NONE	40	8.1	1.9	173	10	66	37
NaH ₂ PO ₂	33	6.0	4.3	238	15	66	39
NaH ₂ PO ₂	40	7.3	4.2	245	16	65	40
NaH ₂ PO ₂	71	7.6	3.9	252	24	66	41
NaH ₂ PO ₂	41	8.2	4.3	237	22	69	40
NaH ₂ PO ₄	34	6.1	3.9	247	18	62	-
NaH ₂ PO ₄	71	7.7	3.1	233	22	62	41
NaH ₂ PO ₄	50	10.0	4.0	258	25	61	41

Transparency 10

MERCERIZED TWILL

CTLYST	% WPU	% BTCA owf	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
-	-	-	1.3	163	2	100	100
NONE	63	6.8	2.2	217	11	71	126
NONE	43	8.5	2.0	211	8	70	144
NaH ₂ PO ₂	40	7.1	4.0	229	20	69	80
NaH ₂ PO ₂	67	7.2	3.4	272	19	65	84
NaH ₂ PO ₂	46	9.2	3.9	282	25	65	35
NaH ₂ PO ₄	65	5.9	3.4	267	13	71	101
NaH ₂ PO ₄	38	6.8	3.6	263	15	65	81
NaH ₂ PO ₄	68	7.3	2.9	253	17	33	49
NaH ₂ PO ₄	58	11.6	3.6	265	25	66	78

Transparency 11

EFFECTS OF VARYING SOFTENER AFTERTREATMENT

% BTCA owf	SOFTENER	DP	WRA	ACCELERTR % WT LOSS	% STRENGTH RETAINED BREAK	TEAR
------------------	----------	----	-----	------------------------	---------------------------------	------

PRINTCLOTH

7.4	NONE	3.6	269	16	56	42
8.2	PE	3.6	288	14	46	49
8.8	NONION SIL	3.5	309	15	45	48
8.2	CATION SIL	3.5	299	15	47	51

TWILL

10.1	NONE	3.9	229	30	70	34
10.0	PE	4.0	258	25	61	41
10.2	NONION SIL	3.7	287	25	61	40
10.3	CATION SIL	3.5	290	25	61	40

Transparency 12

SUMMARY

- PRIOR MERCERIZATION OF FABRIC CROSSLINKED WITH BTCA TENDED TO PRODUCE BETTER STRENGTH RETENTION BUT POORER DP RATINGS.
- LOW WET PICKUP APPLICATION OF BTCA (AS COMPARED WITH CONVENTIONAL APPLICATION) TENDED TO (1) IMPROVE DP PERFORMANCE OR
(2) MAINTAIN DP PERFORMANCE AT A LOWER APPLICATION LEVEL.

Transparency 13

Dyeability of Cotton Fabrics Treated with Carbamoylethylamine Adducts

Robert M. Reinhardt

Durable press cotton ordinarily is produced by chemical treatment of fabrics with methylolamide compounds which crosslink the cellulose. Conventionally crosslinked cottons exhibit markedly decreased dyeability compared to that of untreated fabric. Interest has grown in the availability of durable press cotton fabrics with enhanced dyeing properties. Two carbamoylethylamine adducts, prepared by reaction of acrylamide and diethylamine or diethanolamine, were investigated as agents to augment the dyeing properties of durable press cottons. The adducts were used, both as simple additives and as methylolated coreactants, along with DMDHEU (dimethyloldihydroxyethyleneurea, the most common durable press agent) in pad-dry-cure finishing treatments. The effects of these adducts in finishing are indicated by chemical analysis, smooth-drying properties, and dyeabilities of the treated fabrics.

Slides used to illustrate the presentation are listed and shown below.

- Slide 1. Title, authors, and acknowledgment.
- Slide 2. Dyeing properties of durable press cottons.
- Slide 3. Adducts of acrylamide and amines; general comments.
- Slide 4. Carbamoylethylamines through reactions of acrylamide with ammonia and amines.
- Slide 5. Preparation of adduct from diethanolamine and acrylamide.
- Slide 6. Methylolation of diethylamine adduct and its reaction with cotton.
- Slide 7. Our investigation of carbamoylethylamines in finishing cotton.
- Slide 8. Laboratory finishing procedure employed.
- Slide 9. DP appearance of cotton printcloth finished with carbamoylethylamines.
- Slide 10. Laboratory dye procedures employed; reactive, direct, and acid dyes studied.
- Slide 11. Color evaluation of dyed samples. Color measurements made on a Milton Roy Color Scan II spectrophotometer.
- Slide 12. Nitrogen analysis of fabrics finished with DMDHEU and hydroxyethyl adduct.
- Slide 13. Dyeabilities of fabrics finished with DMDHEU and hydroxyethyl adduct.
- Slide 14. Dyeabilities of fabrics finished with DMDHEU and ethyl adduct.
- Slide 15. Dyeabilities of fabrics finished with methylolated

adducts alone.

Slide 16. Dyeabilities with Direct Red 79: fabrics finished with DMDHEU and adduct-coreactants.

Slide 17. Dyeabilities with Reactive Red 2: fabrics finished with DMDHEU and adduct-coreactants.

Slide 18. Dyeabilities with Acid Green 25: fabrics finished with DMDHEU and adduct-coreactants.

Slide 19. Summary of findings.

Slide 20. References: earlier work on carbamoylethylamines in finishing.

DYEABILITY OF COTTON FABRIC TREATED WITH CARBAMOYLETHYLAMINE ADDUCTS

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TEXTILE FINISHING CHEMISTRY RESEARCH GROUP
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NEW ORLEANS, LA. 70179

ACKNOWLEDGMENT:

LOUIS J. LAWRENCE, THAOCHI H. CAO, ANASTASIA M. HAMMOND

SLIDE 1

DURABLE PRESS COTTONS

+ ARE ORDINARILY PRODUCED BY CHEMICAL
TREATMENT OF FABRICS WITH METHYLOLAMIDE
COMPOUNDS THAT CROSSLINK THE CELLULOSE.

+ WHEN PROCESSED BY CONVENTIONAL TREAT-
MENTS, EXHIBIT MARKEDLY DECREASED
DYEABILITY COMPARED TO THAT OF
UNTREATED FABRIC.

SLIDE 2

CARBAMOYLETHYLAMINES

ADDUCTS OF ACRYLAMIDE AND AMINES ARE
READILY PREPARED BY THE MICHAEL REACTION

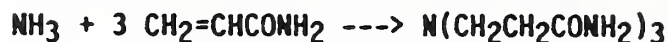
THE PRODUCTS ARE CARBAMOYLETHYLAMINES

STRUCTURES ARE DICTATED BY THE NATURE OF
THE AMINE AND THE RATIO OF REACTANTS

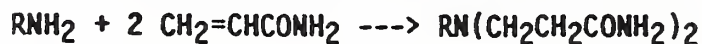
SLIDE 3

CARBAMOYLETHYLAMINE ADDUCTS

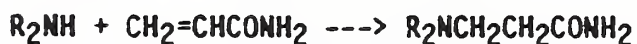
* THROUGH REACTION WITH AMMONIA:



* THROUGH REACTION WITH PRIMARY AMINE:



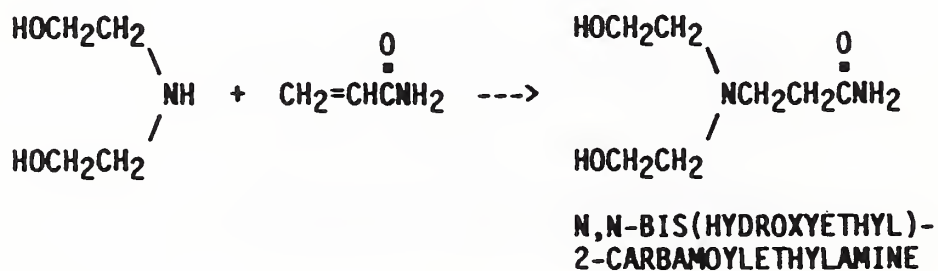
* THROUGH REACTION WITH SECONDARY AMINE:



SLIDE 4

PREPARATION OF ADDUCTS

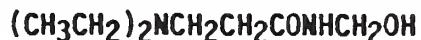
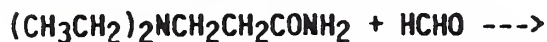
WHEN A SECONDARY AMINE IS USED, THE RESULTING ADDUCT HAS A TERTIARY NITROGEN ATOM WITH A BETA-CARBAMOYLETHYL SUBSTITUENT AND THE TWO GROUPS THAT WERE PRESENT ON THE AMINE.



SLIDE 5

METHYLOLATED ADDUCTS

CARBAMOYLETHYL ADDUCTS CAN BE FURTHER MODIFIED.
THE AMIDE GROUP OF THE ADDUCT CAN REACT WITH
FORMALDEHYDE TO INTRODUCE A METHYLOL FUNCTION
INTO THE COMPOUND.



THE METHYLOLATED ADDUCT CAN REACT WITH CELLULOSE
UNDER THE INFLUENCE OF AN ACIDIC CATALYST.



SLIDE 6

USE OF CARBAMOYLETHYLAMINE ADDUCTS IN FINISHING COTTON FABRICS

- * ADDUCTS AS ADDITIVES IN CONVENTIONAL
TREATMENTS WITH DMDHEU
- * TREATMENTS WITH METHYLOLATED ADDUCTS
ALONE
- * METHYLOLATED ADDUCTS AS COREACTANTS
IN CONVENTIONAL TREATMENTS WITH DMDHEU

SLIDE 7

LABORATORY FINISHING PROCEDURE

COTTON PRINTCLOTH PADDED TO 90% PICKUP OF
SOLUTION CONTAINING:

6% DMDHEU (CROSSLINKING AGENT)
1.8-3.6% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (CATALYST)
0-6% ADDUCT AS ADDITIVE, OR
METHYLOLATED ADDUCT AS COREACTANT

MOUNTED ON PIN FRAME

DRIED IN HOT AIR OVEN FOR 7 MIN. AT 65°C

CURED IN HOT AIR OVEN FOR 3 MIN. AT 160°C

WASHED AND TUMBLED DRIED

SLIDE 8

DURABLE PRESS APPEARANCE OF COTTON PRINTCLOTH

TREATMENT	DP RATING
UNTREATED	1.0
DMDHEU	2.8-3.5
DMDHEU + ADDUCT	3.4-3.5
METHYLOLATED ADDUCT	1.0-2.5
DMDHEU + METHYLOLATED ADDUCT	3.2-4.3

SLIDE 9

LABORATORY DYE PROCEDURE

- * DYE BATH:

REACTIVE RED 2 ----- 3% DYE (OWF) 1% WET. AGENT	DIRECT RED 79 ----- 3% DYE (OWF) 20% SALT 1% WET. AGENT	ACID GREEN 25 ----- 3% DYE (OWF) 1% WET. AGENT
--	---	---
- * BATH ADJUSTED TO pH 3
- * LIQUOR TO FABRIC RATIO, 20:1
- * DYE AT 95°C FOR 60 MINUTES IN AHIBA POLYMAT MACHINE
- * RINSE WITH COLD WATER FOR 15 MINUTES
- * WASH WITH HOT WATER FOR 15 MINUTES
- * DRY

SLIDE 10

COLOR EVALUATION

KUBELKA-MUNK EQUATION:

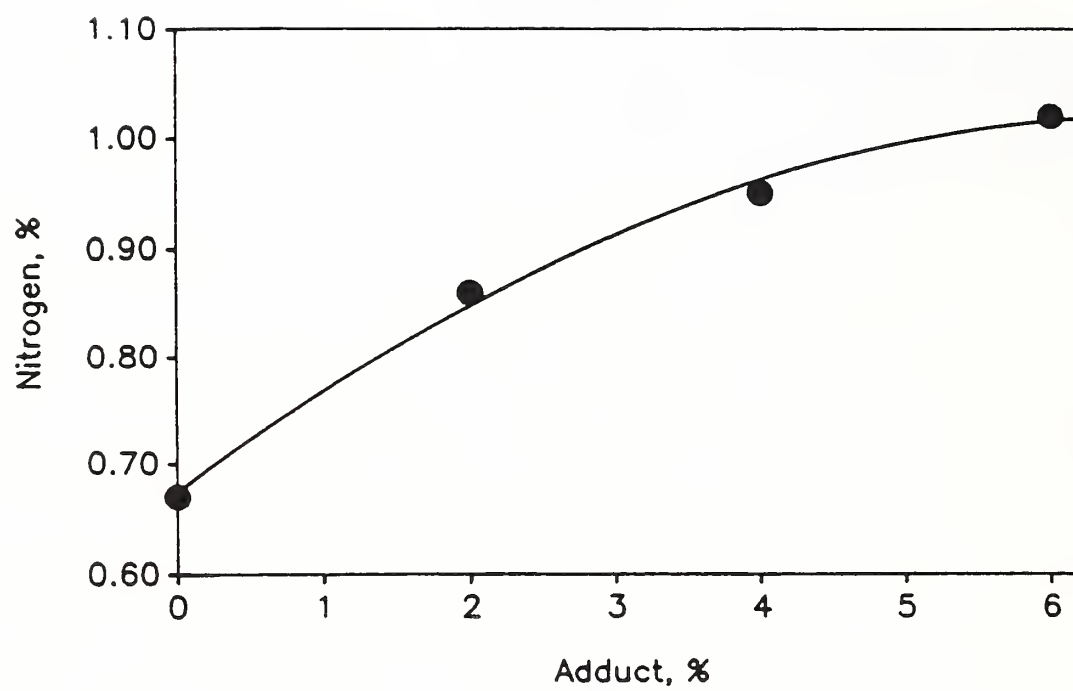
$$K/S = (1-R)^2/2R$$

K IS ABSORPTION COEFFICIENT

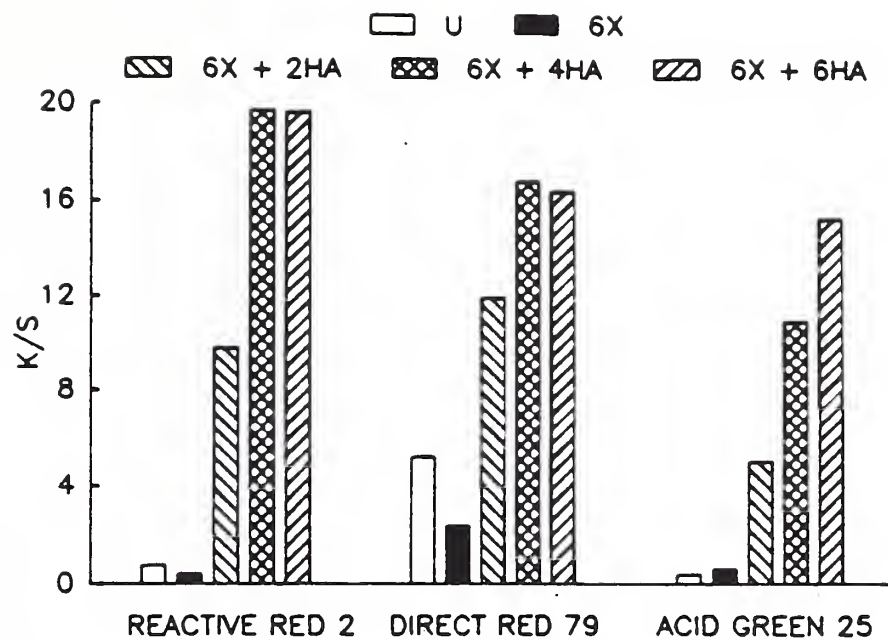
S IS SCATTERING COEFFICIENT

R IS REFLECTANCE AT WAVELENGTH OF MAXIMUM ABSORPTION

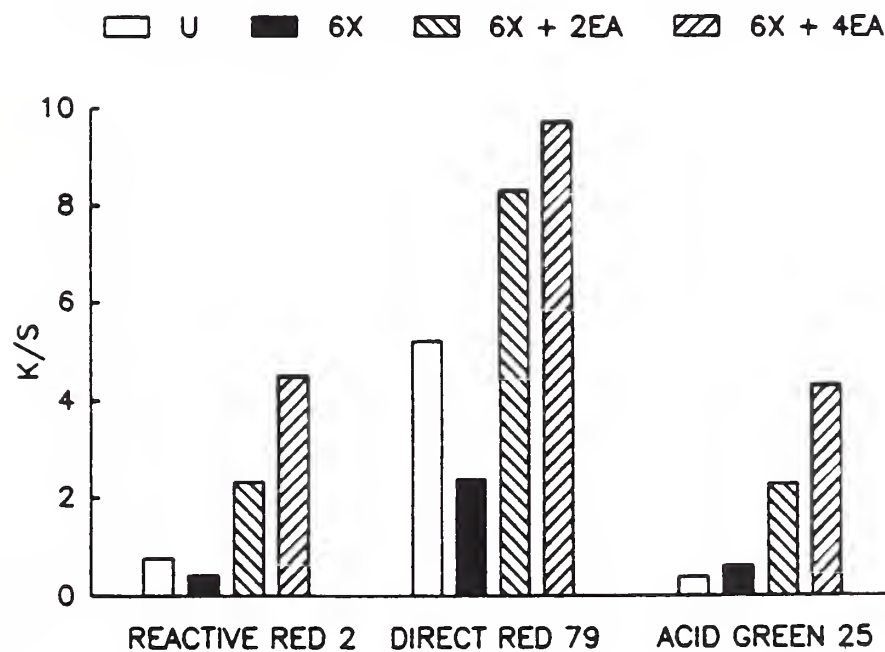
SLIDE 11



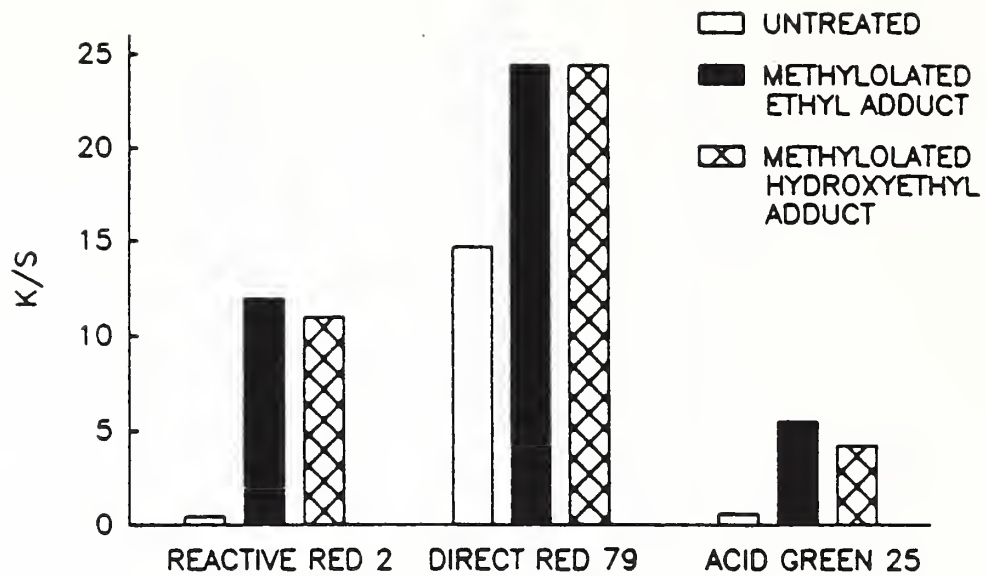
SLIDE 12



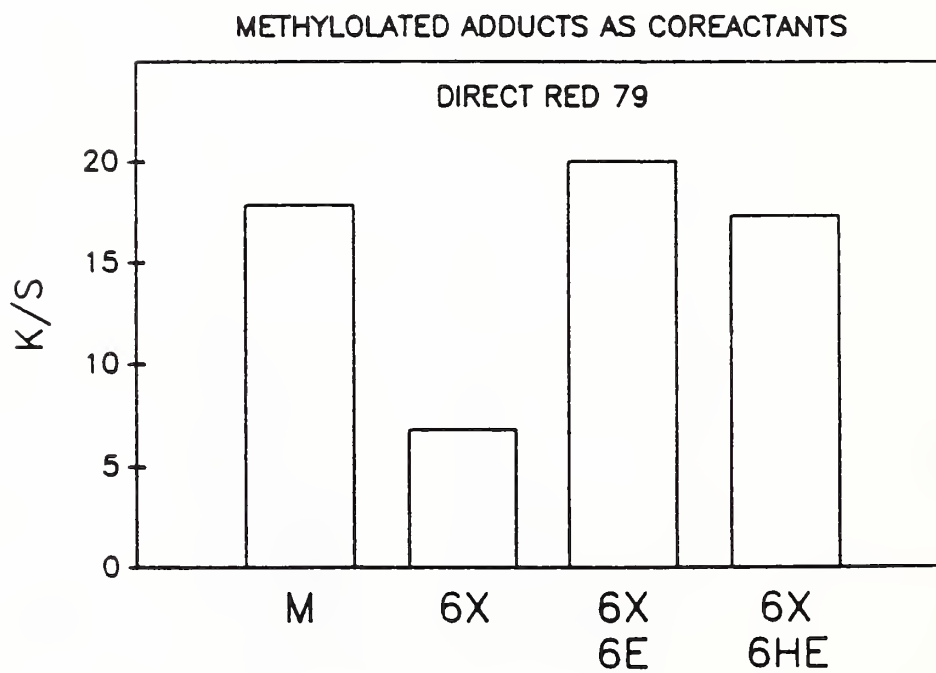
SLIDE 13



SLIDE 14

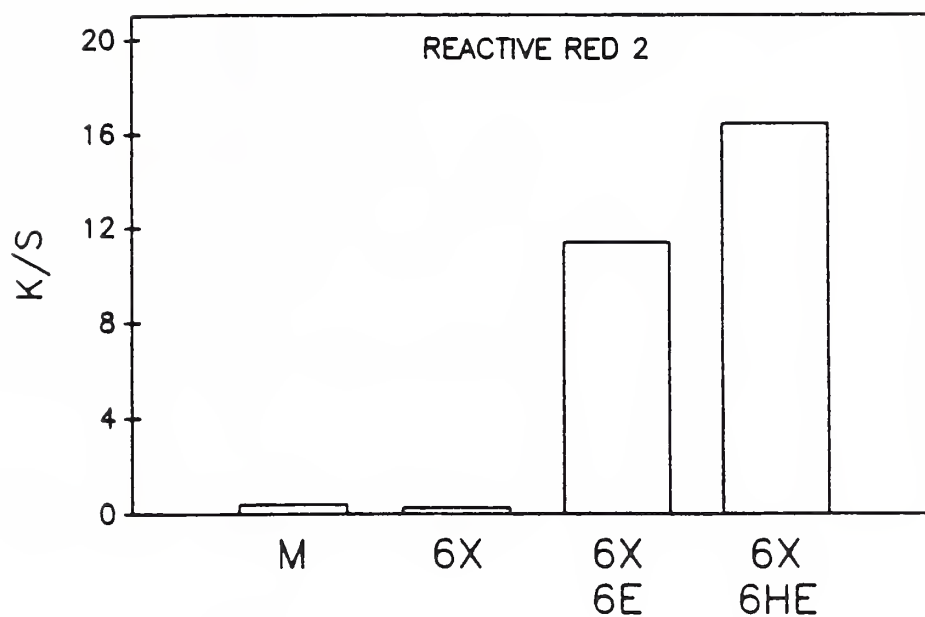


SLIDE 15



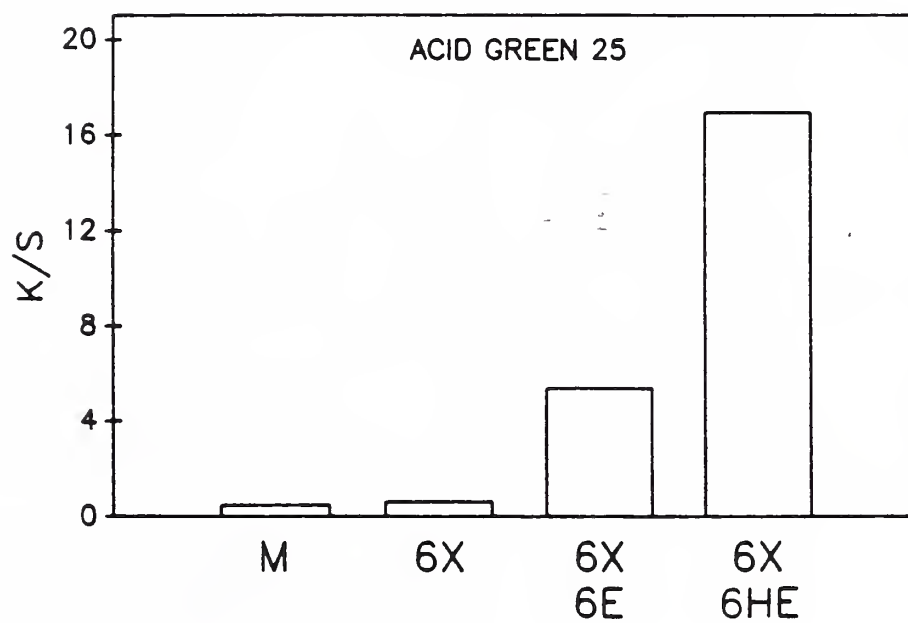
SLIDE 16

METHYLOLATED ADDUCTS AS COREACTANTS



SLIDE 17

METHYLOLATED ADDUCTS AS COREACTANTS



SLIDE 18

SUMMARY

- * DIETHYLAMINE-ACRYLAMIDE AND DIETHANOLAMINE-ACRYLAMIDE ADDUCTS CAN BE USED AS ADDITIVES IN FINISHING COTTON WITH DMDHEU TO GIVE FABRICS WITH DURABLE PRESS PROPERTIES AND ENHANCED DYEABILITIES. THE ADDITIVES BECOME PART OF THE FINISH. THE FABRICS, UNLIKE CONVENTIONALLY CROSSLINKED COTTONS, ARE READILY DYED WITH REACTIVE AND DIRECT DYES. IN ADDITION, THEY CAN BE DYED WITH ACID DYES.
- * METHYLATION OF THE ADDUCTS RENDERS THEM REACTIVE TO CELLULOSE. USED ALONE TO FINISH COTTON THEY SIMILARLY MODIFY THE DYEING PROPERTIES BUT DO NOT PRODUCE WRINKLE RESISTANCE.
- * THE METHYLOLATED ADDUCTS CAN BE USED AS COREACTANTS WITH DMDHEU IN FINISHING. THE TREATED FABRICS HAVE DURABLE PRESS PROPERTIES AND ARE DYEABLE WITH REACTIVE, DIRECT AND ACID DYES.

SLIDE 19

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- FRICK, J.G., JR., ANDREWS, B.A.K. AND REID, J.D., DURABLE WASH-WEAR FINISHES FOR COTTON, AM. DYESTUFF REPTR. 51 (23), 45-48 (1962).
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- VAIL, S.L., REINHARDT, R.M. AND FENNER, T.W., METHYLOLAMIDES CONTAINING AMINO ACID GROUPS: THEIR USE AS WASH-WEAR FINISHING AGENTS FOR COTTON, J. APPL. POLYMER SCI. 9, 1757-1766 (1965).

SLIDE 20

RECENT ADVANCES IN THE USE OF AMINE ADDITIVES
TO IMPROVE DYEABILITY OF CROSSLINKED COTTON

GENE J. BLANCHARD

Hydroxyalkylamines are effective additives for improving the dyeability of crosslinked cotton. Some of the amines that have been investigated are shown in Slide 1. These amines can be either primary, secondary, or tertiary types. Because such compounds are highly basic, they must be neutralized prior to incorporating them in the crosslinking formulation. This is accomplished through formation of the amine hydrochloride, in which case the amine is reacted with HCl, as shown in Slide 2. The amine hydrochloride can be isolated, but a concentrated stock solution is usually prepared to facilitate formulation preparation.

During the crosslinking of cellulose, the amine is free to react with dimethyloldihydroxyethyleneurea (DMDHEU) crosslinking agent. It then becomes permanently bound to the cellulosic substrate (Slide 3). If the amine is multifunctional, numerous opportunities for reaction with the crosslinking agent exist. After the finishing treatment, the cellulosic material can be dyed even though it is crosslinked. In Slide 4 the dyeing conditions are described. The most important step is the adjustment of the dyebath pH to approximately 3-4 in order to properly protonize the nitrogen atom. The classes of dyes that can be used for dyeing the DMDHEU crosslinked cotton are acid, direct, and reactive dyes (Slide 5). All of these dyes are anionic dyes with sulfonate anions, which can interact with the positively charged nitrogen.

The size of the dye molecule is an important consideration because too large a dye molecule can result in difficulty in penetration of the crosslinked cellulosic structure. After dyeing, color strength is evaluated with a spectrophotometer according to the Kubelka-Munk equation (Slide 6). The affect of pH on dyeability of crosslinked cotton with an acid dye is seen in Slide 7. The crosslinked cellulose can be dyed with anionic dyes under the proper pH conditions. Those fabrics that were dyed at pH of 3-4 had the best color strength. These same results were obtained with other classes of anionic dyes. Comparisons of color strength and fastness properties of fabrics finished with DMDHEU crosslinking agent and primary, secondary, and tertiary amines, and then dyed with low, medium, and high molecular weight direct dyes are shown in Slides 8, 9, 10. The properties were best for fabrics treated with secondary (DEA) and tertiary (TEA) amines. Overall, the best additive for improving the dyeability of crosslinked cotton was triethanolamine (TEA). Color strength and wash fastness of fabrics dyed with Direct Red

81, 79, and 80 are summerized in Slide 11. Generally, fabrics that were dyed with the higher molecular weight dyes had the best fastness properties.

Also in this study, the dyeing and physical properties of fabric crosslinked with DMDHEU in the presence of triethanolamine were compared to those of cellulose treated with crosslinking agent in combination with hydroxyethyl derivatives of morpholine, piperazine, and pyrrolidine. These cyclic tertiary amines are illustrated in Slide 12. Physical properties of fabrics finished with 6% DMDHEU and 6% amine additive are shown in Slide 13, and a comparison of the dyeing properties is seen in Slide 14.

**HYDROXYALKYLAMINE ADDITIVES USED IN REACTION
OF CELLULOSE WITH DMDHEU TO PRODUCE DYEABLE
SMOOTH DRYING COTTON FABRICS**

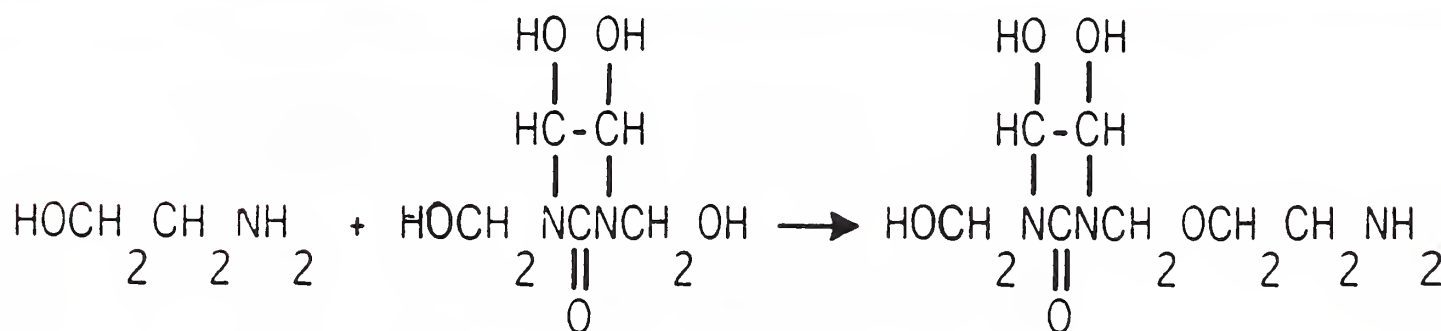
Amine	Structure	MW
MONOETHANOLAMINE	$\text{HOCH}_2\text{CH}_2\text{NH}_2$	61.1
DIETHANOLAMINE	$(\text{HOCH}_2\text{CH}_2)_2\text{NH}$	105.1
METHYLDIETHANOL- AMINE	$(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_3$	119.2
PHENYLDIETHANOL- AMINE	$(\text{HOCH}_2\text{CH}_2)_2\text{NC}_6\text{H}_5$	181.2
TRIETHANOLAMINE	$(\text{HOCH}_2\text{CH}_2)_3\text{N}$	149.2

FORMATION OF AMINE HYDROCHLORIDE



MP. 177-179°C

REACTION OF ETHANOLAMINE WITH DMDHEU



SLIDE 3

DYEING CONDITIONS

LIQUOR-FABRIC RATIO 20:1

4% DYE (BASED ON FABRIC WT.)

20% NaCl (EXCEPT WITH SOME DYES)

1% NON-IONIC WETTING AGENT

pH ADJUSTED TO 3-4

DYEING TIME : 30-60 MIN.

DYEING TEMP : 95 DEG C.

**CLASSES OF DYES THAT CAN BE USED
FOR DYEING COTTON CROSSLINKED WITH
DIMETHYLOLDIHYDROXYETHYLENEUREA
(DMDHEU)
IN THE PRESENCE OF HYDROXYALKYLAMINE**

201

- 1. ACID - AZO, AZINE, etc. ($R-SO_3Na$)
(MOLECULAR WT.= 400-800)**
- 2. DIRECT - AZO COMPS. ($R-SO_3Na$)
(MOLECULAR WT.= 600-1300)**
- 3. REACTIVE - MONO, DICHLOROTRIAZINE**

COLOR STRENGTH EVALUATION

KUBELKA-MUNK EQUATION

$$K/S = (1-R)^2/2R$$

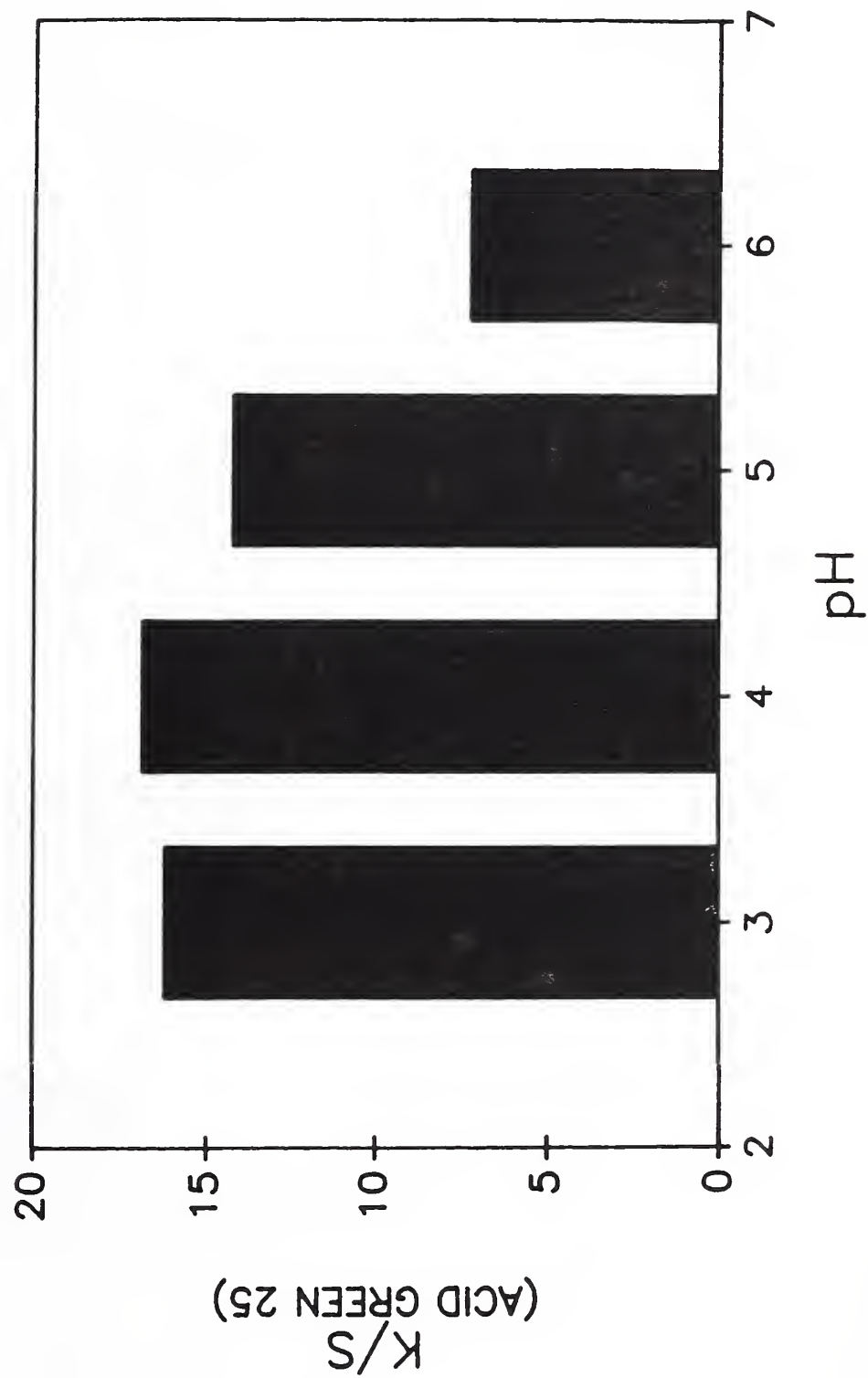
202

K : ABSORPTION COEFFICIENT

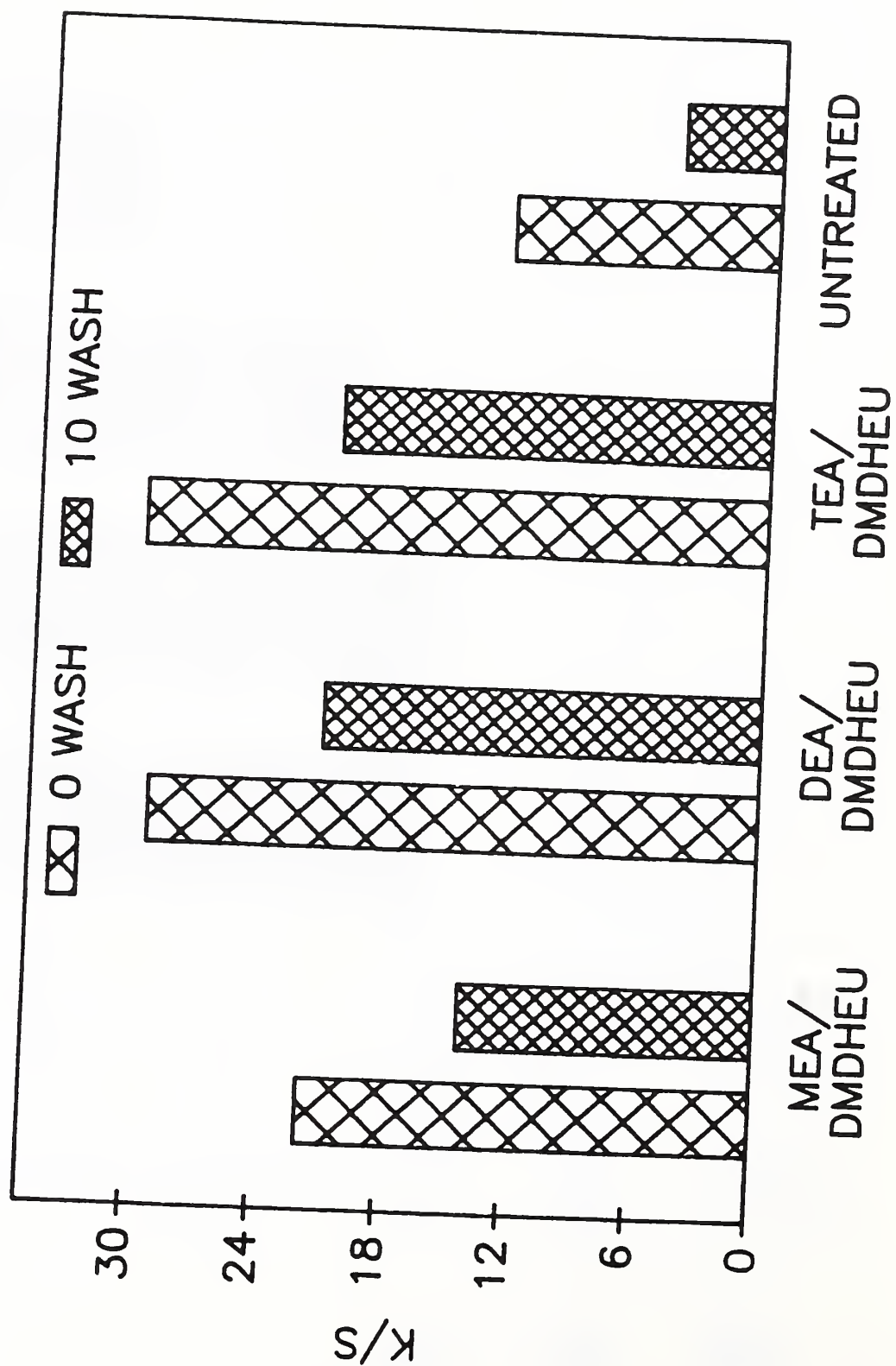
S : SCATTERING COEFFICIENT

**R : REFLECTANCE AT WAVELENGTH
OF MAXIMUM ABSORPTION**

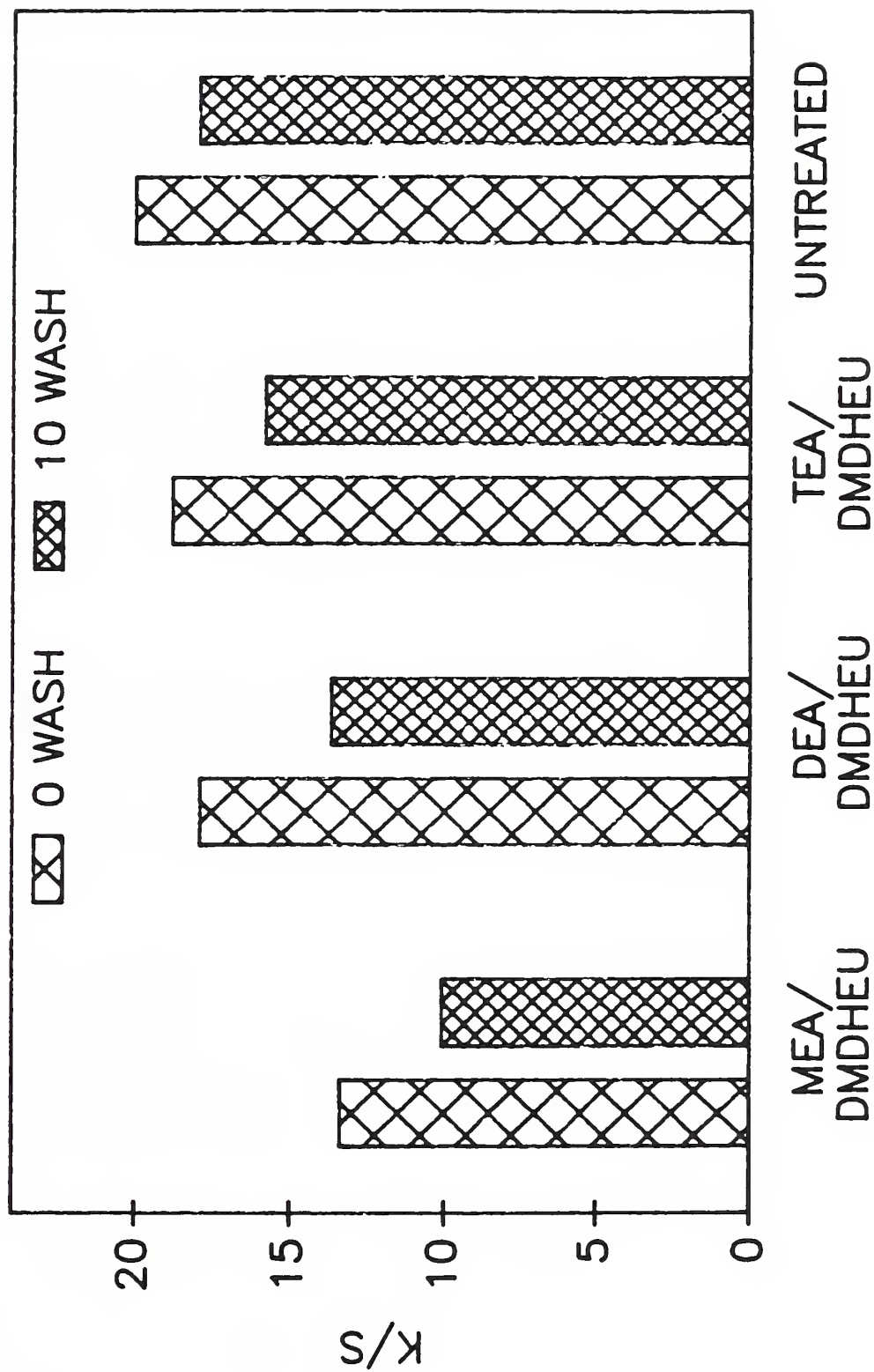
EFFECT OF pH ON DYEABILITY OF COTTON
FINISHED WITH 6.4% TEA·HCl AND 5% DMDHEU



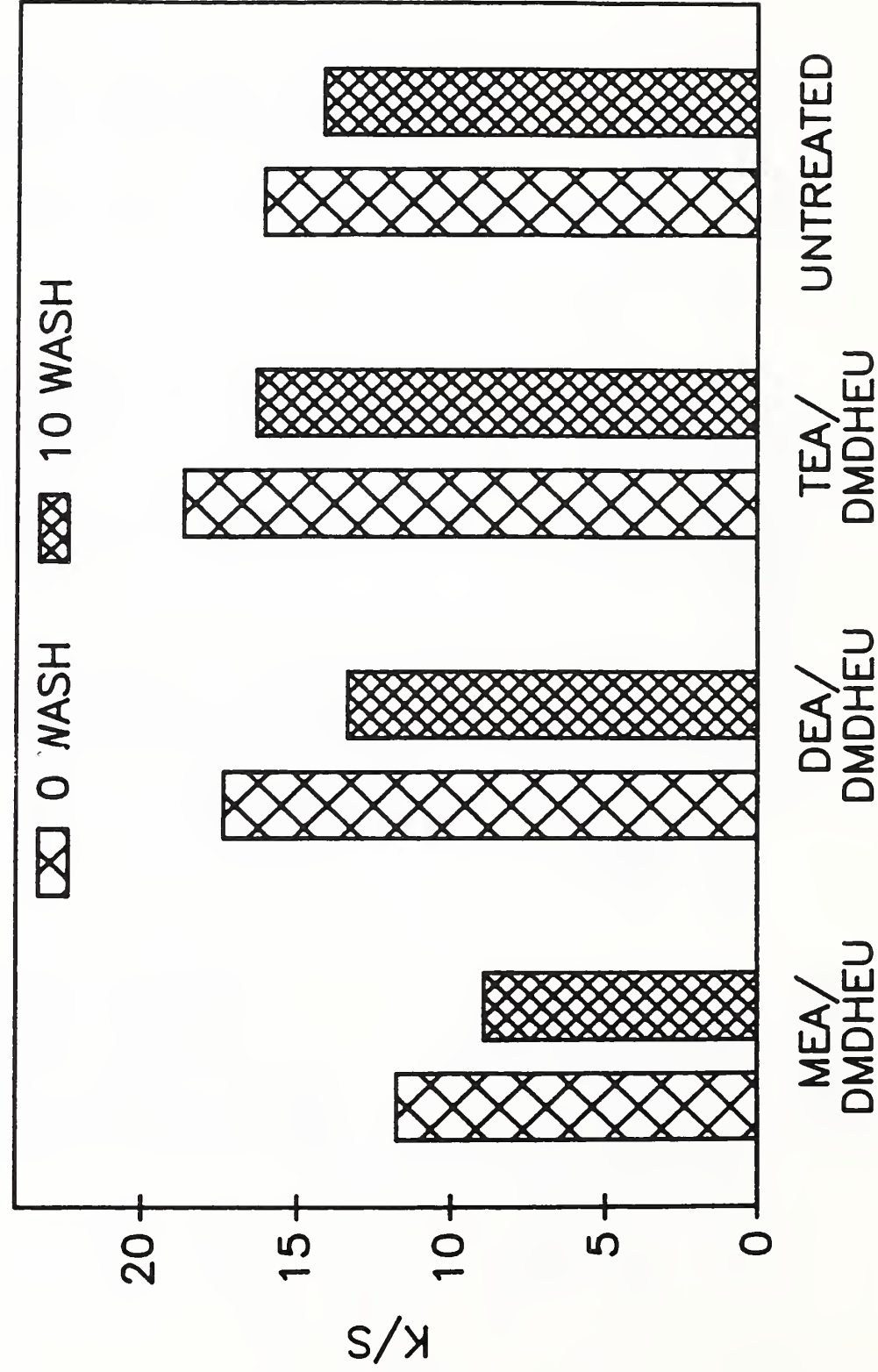
COTTON PRINTCLOTH
DYED WITH 4% DIRECT RED 81



COTTON PRINTCLOTH
DYED WITH 4% DIRECT RED 79

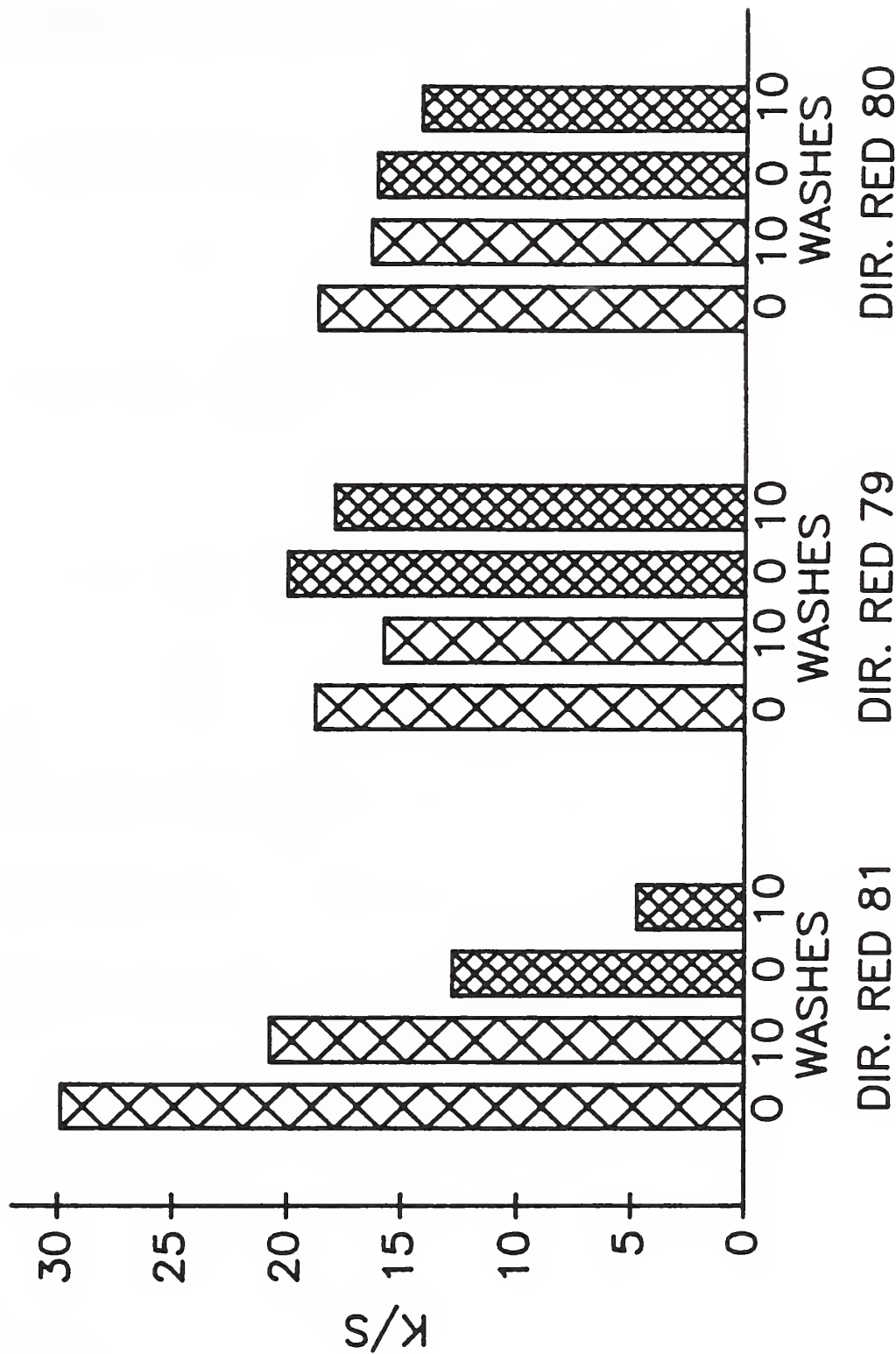


COTTON PRINTCLOTH DYED WITH 4% DIRECT RED 80



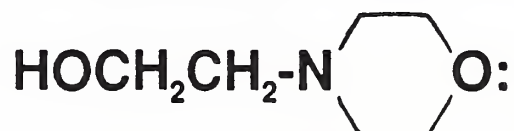
COLORFASTNESS OF COTTON PRINTCLOTH

 DMDHEU/TEA TREATED
  UNTREATED

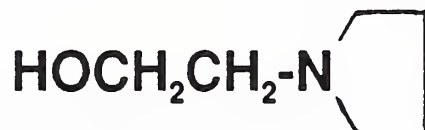


HYDROXYALKYLAMINES

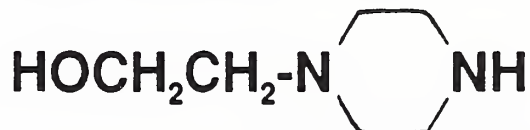
4-(2-Hydroxyethyl)morpholine



1-(2-Hydroxyethyl)pyrrolidine



1-(2-hydroxyethyl)piperazine



1,4-bis(2-Hydroxyethyl)piperazine



4-(2-Hydroxyethyl)-1-piperazineethane-sulfonic acid



SLIDE 12

PROPERTIES OF FABRIC FINISHED WITH 6% DMDHEU AND 6% HYDROXYALKYL AMINE.

AMINE ADDITIVE	Break. Str. (W), % Ret.	Tear. Str. % Ret	WRA (Cond.) (W+F), Deg.	DP Rating
HOEt-MORPHOLINE	75	72	242	3.4
HOEt-PYRROLIDINE	52	58	266	3.5
HOEt-PIPERAZINE	75	71	243	3.0
BIS (HOEt) -PIPERAZINE	71	69	240	3.5
HOEt-PIPERAZINE- ETHANESULFONIC ACID	67	68	258	3.3
TRIETHANOL AMINE	58	59	279	3.8
DMDHEU CONTROL	55	60	279	4.0
UNTREATED COTTON	100	100	198	1.0

SLIDE 13

PROPERTIES OF FABRIC FINISHED WITH 6% DMDHEU AND 6% HYDROXYALKYL AMINE

AMINE ADDITIVE	N %	CIE WI	K/S VALUES			
			DIRECT RED		REACT. RED	
			81	79	80	2
HOEt-MORPHOLINE	0.8	48	7	17	17	13
HOEt-PYRROLIDINE	0.9	43	29	21	20	30
HOEt-PIPERAZINE	1.0	-52	11	21	19	23
BIS (HOEt) -PIPERAZINE	1.0	33	15	21	20	24
HOEt-PIPERAZINE- ETHANESULFONIC ACID	0.8	76	4	11	8	0.4
TRIETHANOL AMINE	0.9	72	20	18	14	27
DMDHEU CONTROL	0.7	77	5	5	2	0.2
UNTREATED COTTON	0.0	88	4	13	11	0.2

SLIDE 14

SUMMARY

Hydroxyalkylamines are effective as additives for improving the dyeability of cotton crosslinked with DMDHEU. The classes of dyes that can be used for dyeing the DMDHEU crosslinked cotton are acid, direct, and reactive dyes. Adjustment of dyebath pH to approximately 3-4 is required for efficient dyeing in order to properly protonize the nitrogen atom .

Although primary, secondary, and tertiary amines can be used for dyeing crosslinked fabric, the best results were obtained with tertiary triethanolamine with respect to color strength and wash fastness. The molecular size of the dye is important because too large a dye molecule can result in difficulty in penetration of the crosslinked cellulosic structure.

Hydroxyethyl derivatives of morpholine, piperazine, and pyrrolidine are effective in enhancing the dyeability of crosslinked cotton, but these fabrics show some discoloration upon curing, as indicated by the whiteness index.

CURRENT STATUS OF RESEARCH ON COTTON NONWOVENS

Jerry P. Moreau

Prospects for increased use of cotton fiber in the nonwovens fabric industry are encouraging. There is need for research on cotton nonwoven fabrics in order to evaluate fabric properties and report technical data. Such is the objective of the project initiated at SRRC, ARS, USDA in New Orleans, LA.

In initial experiments, thermally bonded cotton\polypropylene blended fabrics were compared to a 100% PP fabric. Results showed that strength properties decreased as the amount of cotton increased. However, the high cotton blended fabrics showed less stiffness, a greater cover factor, and faster wicking. Opening and blending evaluations were also conducted. Results indicated that preparation of the most uniform batt was obtained when cotton and polypropylene fibers were opened separately in a Rando Opener/Cleaner, blended in a beater box, then formed into a lap before carding to deliver the batt.

Other experiments were conducted to determine the relative quality and processability of eight cotton samples. Bleached cottons with and without lubricant finishes gave a greater number of neps and greater fiber friction in the nonwoven web than did raw or gray cotton. This indicates that bleached cottons were more readily damaged by processing and demonstrates a need for improved lubricants that will match the performance of raw or gray cotton containing natural waxes. Evaluation of yarns prepared from these eight fibers gave more dramatic differences in properties. In general, yarn from bleached cottons without a lubricant finish were the most difficult to process and gave a poorer quality yarn. The lubricant-treated bleached cottons (#5, #6, #7, #8) performed better in every category than did the unfinished bleached cotton (#4). Strength properties of yarns from finished cottons were even better than raw (#1) and gray (#2) cottons. However, subjective processability (carding and spinning) of finished bleached cottons was not as good as raw and gray cottons.

Nonwoven fabrics were prepared by thermal bonding on a two-roll calender. Fabrics of 70/30 C/PP, 25/75 C/PP, and 100% PP were prepared at 40g/m², 60g/m², and 80g/m² each at various bonding temperatures. Breaking strength, stiffness, and biodegradation data were presented.

ACKNOWLEDGEMENT

The author thanks Gordon Boudreaux and Tom Gentry for laboratory technical assistance.

LIMITATIONS OF COTTON FOR USE IN NONWOVENS

PRESENCE OF NON-FIBROUS MATERIALS

Cleaned to remove trash

Bleached to remove wax, etc.

SLOWER PROCESSING SPEEDS IN CARDING

FIBER DAMAGE IN PROCESSING

SHORTER STAPLE LENGTH

NON-UNIFORMITY

Lack of a consistent product

LACK OF MARKETABILITY

LACK OF DEMONSTRATED TECHNICAL FEASIBILITY

RESEARCH APPROACH

1. USE A MINIMUM OF 50% COTTON IN ALL NONWOVEN SYSTEMS.
2. THERMAL BONDING WITH CALENDER ROLLS WILL BE THE MAJOR BONDING TECHNIQUE FOR PROVIDING FABRIC INTEGRITY.
3. DETERMINE THE "BEST" SYNTHETIC FIBER FOR BLENDING WITH COTTON.
4. DETERMINE OPTIMUM BLEND LEVELS FOR FABRICS DIRECTED TOWARD A PARTICULAR APPLICATION.
5. INVESTIGATE OPTIMUM BONDING TEMPERATURES.
6. PREPARE PRODUCT-ORIENTATED COTTON BLEND FABRICS.
7. DETERMINE PROPERTIES: Comfort-Hand-Feel, Strength, Absorbency, Biodegradability, etc.
8. INVESTIGATE FIBER PREPARATION (OPENING & BLENDING) AND WEB FORMATION.
9. DETERMINE RELATIONSHIP OF COTTON FIBER PROPERTIES TO PROCESSING AND TO FINISHED NONWOVEN FABRIC PROPERTIES.
10. INVESTIGATE THERMAL BONDING BY HOT AIR CONVECTION USING HIGH LOFT WEBS.
11. INVESTIGATE HYDROENTANGLEMENT.
12. INVESTIGATE NEEDLEPUNCHING.
13. COOPERATE WITH FIBER PRODUCERS AND EQUIPMENT MANUFACTURERS.

UNIFORMITY EVALUATION - C/PP BATTS¹

		<u>AVERAGES</u>	
<u>OPENING</u>	<u>BLENDING</u>	<u>REFLECT.</u>	<u>% C. V.</u>
1. C - Spinlab PP - Spinlab 2x	None	75	8.96
2. C - Card PP - Card	Card	76	7.78
3. C - Spinlab PP - Cleaner	Spinlab	81	7.54
4. C - Spinlab PP - Spinlab 2x	Spinlab	72	7.28
5. C/PP-Hopper	Hopper	77	5.61
6. C/PP-Hopper	Rando batt	69	4.81
7. C - Cleaner PP - Cleaner	Spinlab	67	6.77
8. C - Cleaner PP - Cleaner	Beater 1x/Lap	71	4.59
9. C - Cleaner PP - Cleaner	Beater 2x/Lap	72	3.35

¹ Bleached Cotton/black Polypropylene - (C/PP) 80/20;
Batt (18" X 36"; 45 g/m) prepared on card.

ANALYSES OF COTTON FIBERS

Fiber	Fine- ness	Maturity %	Tensile Str. g/tex	Elong. %	Mean Length, inches	Short Fiber, %
1. Raw	242	90.7	17.2	5.3	0.64	36.5
2. Gray	239	92.0	16.8	5.8	0.62	36.9
3. Bleached	233	92.8	17.9	4.3	0.64	35.5
4. Bleached	225	94.4	16.4	4.5	0.63	36.9
5. 0.25% BES*	246	88.5	16.7	5.0	0.60	41.1
6. 1% BES*	222	95.6	15.6	5.0	0.62	38.7
7. 1% Sonostat*	239	89.4	15.9	5.0	0.64	35.4
8. 0.5% Dow 1111*	232	90.6	14.0	4.5	0.62	37.2

*Finish applied to bleached cotton fiber

ANALYSES OF COTTON FIBERS

<u>Fiber</u>	<u>Neps/ gm</u>	<u>Shear Friction, H</u>
1. Raw	224	0.7683
2. Gray	329	0.7778
3. Bleached	602	1.8508
4. Bleached	556	1.0979
5. 0.25% BES*	810	1.2807
6. 1% BES*	495	1.2894
7. 1% Sonostat*	674	0.9353
8. 0.5% Dow 1111*	643	1.1592

*Finish applied to bleached cotton fiber

ANALYSIS OF COTTON YARNS

YARN ¹	CARDING		SPINNING		SINGLE END	
	Comments	Waste, %	Comments	Yards	Bk. Str. Tenacity gms	B.S./Tex
1. Raw	Good	5.2	Good	1250	268	9.8
2. Gray	Good	4.4	Good	1220	266	9.5
3. Bleached	Difficult	30.7	No yarn	No yarn	---	---
4. Bleached	Poor	4.8	Many breaks	800	252	8.7
5. 0.25% BES ²	Good	3.6	OK; breaks	1070	317	11.3
6. 1% BES ²	Good	4.4	OK; break	1200	308	11.1
7. 1% Sonostat ²	Good	4.6	OK; break	1200	268	9.6
8. 0.5% Dow 1111 ²	Good	4.0	Good	1200	315	11.2

¹ Fibers used to prepare 22/1 ring spun yarn

² Finish applied to bleached cotton fibers

ANALYSES OF COTTON YARN

USTER EVENNESS TEST

<u>YARN¹</u>	<u>Yarn Grade</u>	<u>%CV</u>	<u>THIN</u>	<u>THICK</u>	<u>NEPS</u>
1. Raw	C-	25.5	1208	1808	280
2. Gray	C	26.7	1528	2112	360
3. Bleached	--	---	---	---	---
4. Bleached	D+	36.1	5360	4000	904
5. 0.25% BES ²	D	34.0	4040	3184	768
6. 1% BES ²	C	29.9	1984	2072	208
7. 1% Sonostat ²	C	29.9	2624	2536	296
8. 0.5% Dow 1111 ²	C-	30.7	2648	2488	372

¹ Fibers used to prepare 22/1 ring spun yarn.

² Finish applied to bleached cotton fibers.

PHYSICAL PROPERTIES OF NONWOVEN FABRICS AT OPTIMUM BONDING TEMPERATURE

	100% PP	50/50 C/PP	75/25 C/PP
	<hr/>	<hr/>	<hr/>
BREAK. STR. - MD	10.9	4.5	3.2
(lbs-force) - CD	1.7	1.3	0.4
ABRASION, (cycles)	165	118	34
TEAR STR. (gms) CD	160	147	100
BURST. STR. (lbs/in ²)	12.3	10.7	6.3
STIFF. (in.lb.X 10 ⁻⁴)	5.1	6.7	3.8
AIR PERMEABILITY [(ft ³ /min)/ft ²]	356	259	261
WICK. (sec.@ 2&3 cm)	9-21	6-16	6-16

BIODEGRADATION EVALUATION

(ASTM G 21-70)

FUNGI

Aspergillus niger

Penicillium funiculosum

Chaetomium globosum

Gliocladium virens

Aureobasidium pullulans

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